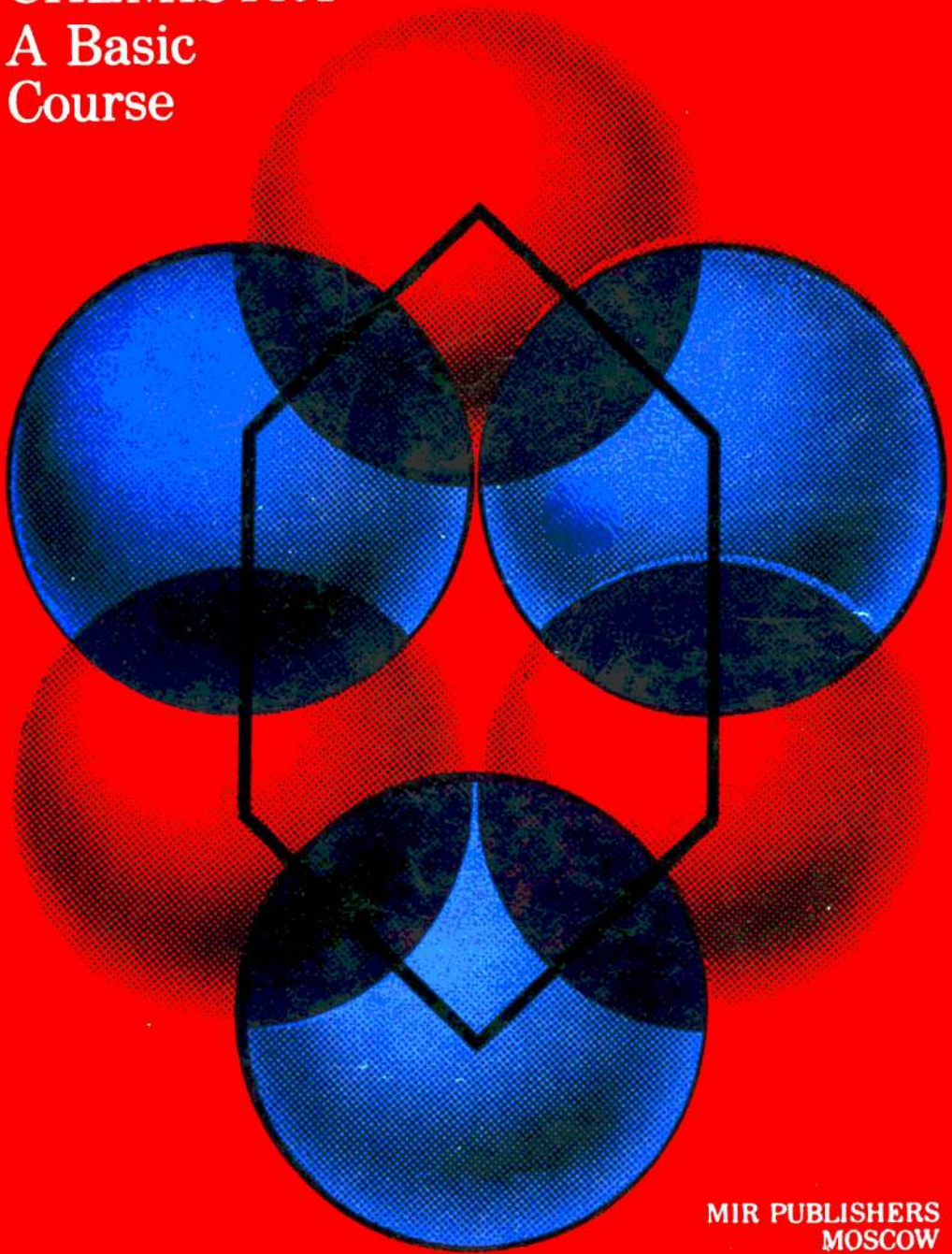
V. V. NEKRASOV

PRACTICAL ORGANIC CHEMISTRY

A Basic Course



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V. V. NEKRASOV

PRACTICAL ORGANIC CHEMISTRY

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МИР

Б. В. НЕКРАСОВ

РУКОВОДСТВО К МАЛОМУ ПРАКТИКУМУ ПО ОРГАНИЧЕСКОЙ ХИМИИ

ИЗДАТЕЛЬСТВО
«ХИМИЯ»
МОСКВА

V. V. NEKRASOV

PRACTICAL ORGANIC CHEMISTRY

A BASIC COURSE

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This book is dedicated to the memory of my late dear teacher Academician Sergei Semenovich Nametkin (1876-1950)

PREFACE TO THE FIFTH RUSSIAN EDITION

As I worked at the fifth edition of this book, I thoroughly revised the former text and made a few abridgements in cases where they seemed necessary.

The theory in many cases was completed with passages that, I think, are essential to keep pace with the modern electronic concepts of the structure of organic compounds and the mechanisms of their reactions.

Vsevolod V. Nekrasov

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INTRODUCTION

Laboratory experiments are an integral part of any syllabus in chemistry, but as the methodology of teaching at higher school has developed it appeared that two main courses are required.

The syllabuses of chemical institutes comprise the major, or full course of practical organic chemistry, which is comparatively large. It offers laboratory experiments that help the student to get acquainted with the methods of synthesizing organic compounds of various classes, and with methods of quantitative elemental analysis. It is quite clear that this full course can be given to students only after the entire course in theory (or at least its major part) has been studied. The synthesis is carried out with comparatively large quantities of substances measured by dozens of grams, and the apparatus used in the experiments are rather cumbersome. The analysis of organic compounds also requires rather complicate equipment.

At the present time there is a strong tendency to give the student a basic, or minor course in laboratory experiments which differs from the major one not only in its scope but the character as well. This course is intended to be given *alongside* with the lectures in theory. The experiments offered in the minor course serve to illustrate the main points of theory given in the lectures, and their main object is to facilitate mastering the theory.

The basic course in practical organic chemistry acquaints the student with the general properties and specific reactions of organic compounds belonging to various classes, and with characteristics of their main most important representatives. Many organic compounds, the properties of which are studied in the basic course, are prepared and isolated in the experiments themselves. Thus, the experiments acquaint the student with some preparative synthesis methods, and also with isolation, purification, and identification of organic substances.

What differs the basic course from its enlarged analogue, is that it deals with small quantities of reagents, measured in grams, and even fractions of a gram, and volumes of the order of 1 to 5 ml. This saves materials and time, and in some cases simplifies the apparatus required to carry out the experiment. The illustrative and methodological value of experimental results is not impaired, where

as small quantities of substances require high accuracy and scrupulous cleanliness on the part of the student and help him train in attention to detail, that will serve him good in his future independent work, whatever it may be. It is, however, seems unnecessary to reduce the volume of reagents to as little as 1-3 drops, since the student will fail to get the proper impression of the general properties of substances and it will be difficult for him to compare these properties and behaviour with those of other substances. Moreover, some operations, such as isolation of substances, their purification, determination of the yields and the main constants, etc., will become impossible with such small quantities of substances, and what will only become evident to the student is the change in the apparent properties of a few drops of the reaction mixture.

The basic course has become the part of the curriculum of almost all higher schools where chemistry is not the main subject, e.g. pedagogical, agricultural, medical, and many others. Laboratory experiments at these institutes are either limited to the scope of the basic course or supplemented with some most important experiments in synthesis or biochemistry. Experiments of the basic course are often the prelude to laboratory work on the main subject, e.g. biochemistry, agrochemistry, pharmaceutical chemistry, chemical technology, etc.

The popularity of the basic course also grows in higher school where chemistry is the main subject, and where the course in theory of organic chemistry is followed by the full course in laboratory experiments (synthesis). The usefulness of the basic course given simultaneously with lectures in theory (parallel courses) has been proved.

The basic course in practical organic chemistry is also the part of the curriculum of vocational and technical schools.

The growing popularity of the basic course is explained also by certain specific features of higher and secondary education in the USSR (e.g. extramural education by correspondence, during which the student works in the laboratory only in the period of examinations, and also education in the evening classes) that set natural limits to the duration of work in the laboratory.

The division of the basic course in practical organic chemistry is as follows:

1. Qualitative observation and study of specific properties and transformations of substances of certain classes. The experiments illustrate and supplement the theory given in lectures.

2. Comparison of properties and transformations of substances having different structure. The experiments show the relation between the chemical structure of the substance and its properties, and teach the student to derive judgement on the structure of a substance from its properties.

3. Synthesis of compounds, their isolation, purification (wherever possible), determination of the yield. These experiments acquaint the student with the methods of preparing organic substances and interconversion of compounds belonging to different classes. The experiments are very important, especially in cases where the student examines the properties and transformations of substances obtained in his own experiments, and uses them in his further work. Quantities of substances used in synthesis may be the same as in the experiments of the full practical course (macro methods), or smaller, measured in a few grams (semimicro methods) or even fractions of a gram (micro methods). Semimicro and micro methods suit the purpose better: they are sufficiently illustrative, the time of the reactions is shorter, consumption of the reagents is reduced, and the apparatus are simpler and compact. In some cases, however, macro methods are used to prepare substances that will be used in further experiments, and are needed in sufficient quantities.

4. Experiments dealing with the simplest methods of isolation and purification of small quantities of organic substances, determination of their molecular mass, physical constants, and qualitative composition.

Laboratory experiments specified under 1, 2, and 3 are grouped into separate chapters according to classes of organic compounds. This division seems to meet the practical demands of the basic course. Each chapter begins with information on substances representing the particular class that will be used in experiments. This information concerns the constants of the substances and, in some cases, the methods of preparing them. Next follows the description of separate experiments. To make the selection of laboratory jobs under 3 easier, titles of these experiments (synthesis) begin with the word 'Preparing'. An example of how to calculate yields of synthesis is given in Experiment 27.

Type 4 experiments should be carried out in the first laboratory jobs; they are therefore given in Chapter 3. The basic practical course usually does not describe general methods for quantitative elemental analysis. Some simplest and special methods of quantitative analysis (determination of acid equivalent weights, ester saponification equivalents, etc.) are given in chapters dealing with compounds of the given class.

The starting materials are specified in each experiment; the exception are substances that are in common use in the laboratory: the information on them is contained in the Appendix. Finally goes the procedure.

In experiments of type 1 and 2, the attention of the student is drawn to the changes in the reaction mixture that are of special importance, e.g. the change in colour, odour, etc.

The description of each experiment (or a group of similar experi-

ments) is followed by the necessary theory, including the modern electronic concepts, and the discussion of the specific features of the experiment, its results and importance.

The number of working hours allotted to the basic course in practical organic chemistry differs depending on the requirements of each particular higher school. The selection of experiments also differs and naturally reflects the importance that is attached to certain classes of organic compounds in a particular higher school. Practical conditions of the laboratory (the availability of certain pieces of equipment and reagents) also influence the scope of experiments and their subject. For this reason, the number of experiments given in the present basic course significantly exceeds the scope of the laboratory work that can be included in a normal curriculum. The abundance of experiments offered in this book helps proper selection of the curriculum for a given higher school or a faculty, or even a particular student.

Experience has shown that many experiments given in the basic course can successfully be used in the full course as well, and even as demonstration experiments.

This book is only a practical manual, and it cannot rival the textbook on organic chemistry. The theory is given in a limited scope and only in cases where it clearly discloses the essence of the experiment. For the same reason the author has not included in this book theoretical problems and exercises or questions, that are often solved or asked during the laboratory work.*

The scope and the character of such exercises and problems depend on the programme of the course in organic chemistry rather than on the type and the subject of the laboratory work.

* See, for instance, Veselovskaya, T. K. and Machinskaya, I. V., *Problems and Exercises in Organic Chemistry*, Rosvuzizdat, Moscow, 1963; Albitskaya, V. M. and Serkova, V. I., *Problems and Exercises in Organic Chemistry*, Vysshaya shkola, Moscow, 1968; Chudny, A. Ya., *Problems and Exercises in Organic Chemistry*, Vysshaya shkola, Moscow, 1969; Kost, A. N., Sagitullin, R. S., and Terentiev, A. P., *Exercises and Problems in Organic Chemistry*, Vysshaya shkola, Moscow, 1974.

CHAPTER ONE

LABORATORY EQUIPMENT

Very simple equipment is required to perform laboratory experiments in the present Basic Course. Almost all operations, including synthesis, can be done on simple laboratory benches having no water taps or sinks.

Apparatus, Glassware, and Other Laboratory Equipment

Each working post should be provided with a stand to hold 10-20 test tubes, and one or two iron stands with clamps and rings. Holders should be secured on the stand so that the rod of the clamp, or ring, rests on the rod support and not on the fixing bolt. The inner surfaces of the clamps should be rubber- or cork-lined to save fragile apparatus such as funnels, condensers, etc. If rubber or cork is not available, asbestos or paper pads can be used instead (see Chapter 2, 'Assembling Apparatus').

Most experiments can be carried out in ordinary test tubes with small quantities of substances, and only some laboratory tasks will require flasks, beakers, porcelain dishes, etc.

In many cases the experiment will require test tubes (see Fig. 1) with inclined side arms (8-20 cm long and 3-5 mm in diameter). These are used for distillation with or without a thermometer (see Experiment 4), as reaction vessels, receptacles of filtrates (filtration with suction, see Experiment 1), receptacles for substances that need protection from atmospheric moisture, and in more complicate apparatus. Common round-bottomed flasks with a side arm (Fig. 9) are used for work with large quantities of reagents.

Test tubes provided with shorter, but wider side arms, slightly pointed upwards (see Fig. 1) are often used to assemble more complicate apparatus.

Vessels with side arms can be manufactured in the laboratory using a blowpipe but usually they can be replaced by a common test tube or a flask with special adapters inserted into their mouth. Adapters are especially convenient in assembling complicate apparatus. For example, a bent tube (Fig. 2*e*) is used in the apparatus for distillation without a thermometer; an open tube with a side arm (Fig. 2*a*),

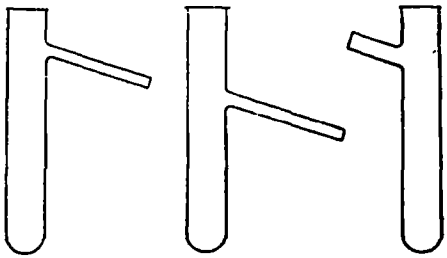


Fig. 1. Test tubes with side arms

for distillation with a thermometer, and a tube with an inclined side arm (Fig. 2*f*) is used when a tubulure is needed. Ordinary glass T-pieces with bent or straight side arms (Fig. 2*b*, *c*) are often used as adapters. Glass tubes with drawn ends (Fig. 2*d*, *g*) are convenient for work with condensers. Glass T-pieces (Fig. 2*a*, *b*, *c*, *f*) provide

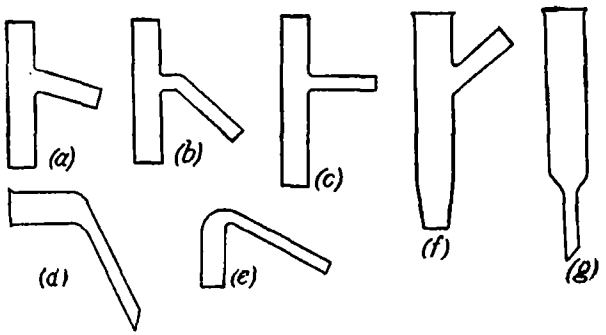


Fig. 2. Adapters

two outlets for a test tube. This is especially important with tubes of small diameters. Using test tubes (flasks) in combination with adapters makes it possible to assemble various apparatus for laboratory experiments of all kinds.

Heating apparatus used in the laboratory are gas or spirit burners.

Spirit burners (glass or metallic) with wicks should be tightly closed with caps to prevent evaporation of alcohol when out of use, and to protect the wick from atmospheric moisture.

If a reaction vessel is to be heated to a temperature not above 100 °C, a water bath is used, which is actually a metallic vessel filled with water. Whenever necessary, the vessel is closed with a tin cover provided with holes to accept test tubes. Sand baths are used to maintain higher temperatures. Only sieved and calcined sand should be used in sand baths. Both water and sand baths are heated

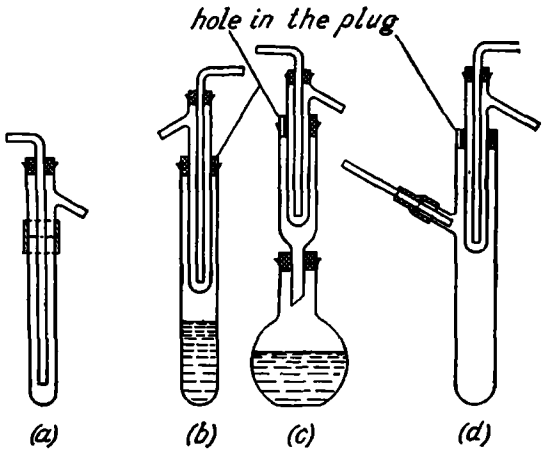


Fig. 3. 'Cold finger' condenser

over burners, or on common electric hotplates. Heating thick-walled glass vessels (e.g. suction flask, see Fig. 6) should be avoided (even on baths).

If a hot reaction mixture or a product of distillation should be quickly cooled, a common glass beaker filled with cold water, and sometimes with snow or crushed ice, can be used.

Various condensers are used to liquefy vapours. Usually these are straight air-cooled tubes (Fig. 8) or tubes enclosed in jackets through which cooling water is circulated (Fig. 9). These can be either straight-run or reflux condensers. In the former apparatus the condensate flows straight into the receptacle, and in reflux condensers the condensed vapour returns into the still as reflux.

In some cases it is convenient to connect the reflux condenser with the reaction vessel through a bent adapter (Fig. 2*d*), and the outlet of the condenser with the receptacle. To simplify the vapour cooling process, a plain tube condenser can be wrapped with filter paper and wetted with water from a wash bottle or a dropping funnel. The dripping water should be collected in a beaker or any other receptacle using a long strip of paper hanging from the condenser. To prevent cooling water from getting into the receptacle, a baffle,

made, for example, from a rubber cap of a penicillin vial, should be put on the lower end of the condenser, below the filter paper wrapping.

It is recommended that a small round opening should be made in the wall of the lower end of a narrow tube of the condenser, adapter, or the outlet tube through which the condensate drips into the receptacle. The hole should be above the condensate level so that air can get inside the system and prevent formation of the liquid column in the tube.

'Cold-finger' condensers are very convenient in many experiments. They are quite effective and require little space on the bench. This is a glass tube sealed on one end (or a long narrow test tube)

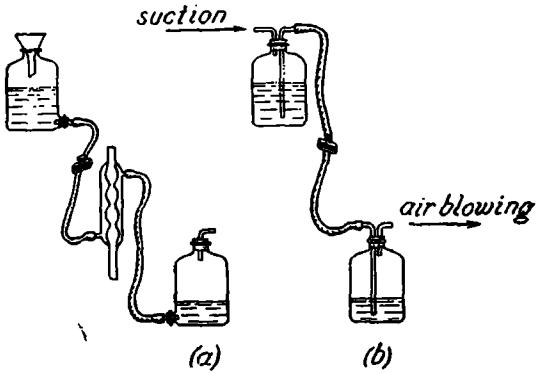


Fig. 4. System for circulating water in condensers (a) and using it as an aspirator (b)

provided with a side arm or an adapter. A narrower tube, almost reaching the test tube bottom, is passed through the plug stoppering the open end (Fig. 3*a*). The direction in which cooling water circulates in such a condenser is not important. If the condenser is connected to the reaction vessel (Fig. 3*b* and *c*) it operates as the reflux condenser, and if the outlet is connected to the receptacle, for instance, a test tube with a tubulure (Fig. 3*d*), it functions as a straight-run condenser.

For a quicker and more effective condensation of vapour, it is recommended that the gap between the cold-finger condenser and the apparatus walls does not exceed 5-10 mm.

Water should be admitted into condensers by gradually opening the tap; otherwise the apparatus can be broken. If water main is absent at the bench, the condenser should be cooled as this. Take two 2-3 litre bottles with tubulures, stopper the tubulures with plugs through which a glass tube is passed, and put rubber tubings, about 1 m long, onto the glass tube ends. Tighten the joints with soft wire or string (Fig. 4*a*). Fill one bottle with water and place on

a shelf over the bench. Fix a screw clip on the rubber tubing, and connect its free end to the lower arm of the condenser. Place the other bottle on the bench and connect to the upper arm of the condenser. Adjust the cooling water flow rate using the screw clip. The flow rate should be low. If all water is drained from the upper bottle before the experiment has been finished, refill it from the lower bottle using a big funnel. If the direction of the water flow does not matter (with condensers shown in Fig. 3), the bottles may be merely changed places and the water flow reversed. True, the temperature of water will slightly rise in this case, but this can be neglected provided the quantities of substances involved in the process are small. When water circulation is no longer necessary, both bottles should be placed on the shelf and their tubings interconnected by a piece of a glass tube.

This simple apparatus can also be used as an aspirator. Accordingly, stopper the upper bottle with a plug through which a tube is passed, and place the lower bottle on a stool or floor to ensure significant difference in liquid levels. As the clip is now released, the system sucks in air with force sufficient, for instance, for filtration (Experiment 1), drying substances with suction, for drying laboratory glass in an air stream, and in other cases where a hand pump or a water-jet ejector would otherwise be necessary. If the lower bottle is now closed with the stopper provided with the tube, and the bottles are changed places, an uninterrupted stream of air can be ensured. Bottles without tubulures can be used as well (Fig. 4*b*). Each bottle should in this case be provided with a stopper through which two tubes are passed, the longer one reaching almost the bottom (siphon) and the shorter ending at the stopper. Water passes from one bottle to the other through the longer tubes. Before using the aspirator, remove air from the tubing connecting the two bottles.

Gases are purified and dried by passing them through a glass tube packed with an absorbing material, mostly calcium chloride or soda lime (see Appendix). The absorbent should be fixed in the tube with loose cotton wool pads on both ends. A guard tube (usually with a drawn end) is installed in the end of the apparatus to protect the reaction mixture from the ingress of atmospheric moisture or when small quantities of harmful gases, such as HCl or HBr, should be absorbed. If the absorption tube has already been used in previous experiments, or exposed to air for a long period of time, check it to see that hydrates or carbonates impermeable to air are not formed in the packing. To that end, blow air through the tube. If the air passes with difficulty, renew the packing. If the air passes but meets some obstacle in its way (i.e. if only a thin dense layer of salts has been formed) loosen the tube packing. To absorb large quantities of such gases soluble in water, connect a funnel to the rubber gas

discharge tube, place the funnel (with its stem upwards) in an inclined position into a beaker containing water, and hold it immersed a few millimeters below the liquid level.

Measure out small portions of solutions and liquid reagents using a pipette (1-10 ml capacity) provided with a narrow tip. The top of the burette can be closed with a finger tip (Fig. 5*a*). Pipettes without graduations, or only with one or two marks, can be manufactured in the laboratory. The marks can be made on strips of

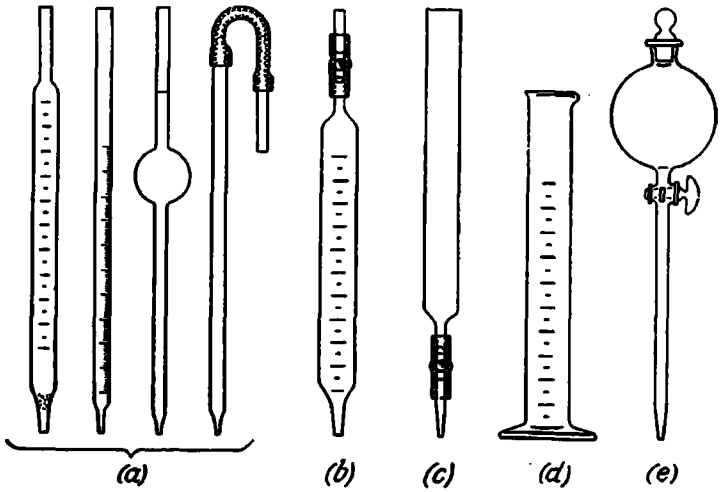


Fig. 5. Volumetric glassware

paper glued to the glass. Pipettes calibrated in 0.1 ml are more convenient. Pipettes are also used for separation of liquids (Experiment 3). Sometimes a long thin-walled rubber tubing is put on the pipette and used to suck in liquids by the mouth. The pipette should be held at the level of the eye so that the meniscus could be followed precisely. A rubber syringe can be used as well, but it is easier to keep the liquid level in the pipette if its top is sealed with a finger.

There is another simple way to seal the pipette on its top. Place a glass bead or a short length of a fused rod inside a soft rubber tubing (Fig. 5*b*) on the pipette top. As the tube is now squeezed between the thumb and the forefinger, narrow channels are formed by the sides of the glass insert and the liquid efflux can thus be controlled. The liquid flow discontinues as soon as the pressure on the rubber tube is released. This seal can be used instead of a clamp in cases where liquid should be discharged in portions.

Smaller measuring cylinders having capacity of 10-15 ml and graduated in 0.1 ml (Fig. 5*d*), or narrow graduated test tubes are convenient for quickly measuring out liquids.

Funnels with stopcocks (Fig. 5*e*), and also burettes with screw clips are used for slow dropwise delivery of liquids.

Ground plugs should be lubricated with Vaseline so that the mating surfaces are clear, but without excess lubricant. Bores in the plugs should be free from the lubricant. To prevent jamming of the plug in the funnel after long storage, a narrow strip of paper should be placed to separate the glass surfaces.

Thermometers filled with mercury, toluene, alcohol, or pentane are used in many laboratory experiments. Thermometers graduated in 1 °C to 100, 250 or 360 °C are most popular. They should be checked at least at two points, by measuring the temperature of a snow (ice) mixture with water (0 °C) and of boiling water (100 °C). (The corresponding mark on the scale should lie close to the liquid level.) This simple test shows that corrections should be introduced into readings of some thermometers. Corrections may vary for different parts of the scale, increasing towards the region of higher temperatures. They can be determined experimentally by measuring the melting points (Experiment 7) or boiling points (Experiment 10) of pure substances, the constants of which correspond to the temperatures checked. The found correction should be written down on the thermometer case (see also explanations to Experiments 4-12).

The chemical laboratory should be equipped with several chemical balances (maximum load 200-500 g, sensitive to 0.05-0.01 g) and sets of weights. Glass and rubber tubes, glass rods, stoppers (rubber and cork), a cork press, stopper drills, test tube holders, bottle brushes, test tube stands with pegs, towels, scissors, files, spatulas, glass-writing pencils, tongs, gauzes with asbestos-filled centres should also be available in the laboratory.

Filtration and distillation apparatus, devices for drying crystals with suction, and for separating layers of liquids, and also methods how to handle these and other general operations will be described in Chapter 3.

Reagents and Materials

The composition and properties of various substances that will be used in experiments described in Chapters from 3 to 21, and sometimes methods of preparing them, will be given at the beginning of each chapter. The preamble to each experiment specifies also the materials, starting substances, and special reagents that are necessary to carry out the experiment. Many reagents, acids and alkalis in particular, are used in most experiments, and should therefore always be available in the laboratory. Their composition and methods of preparing are given in the Appendix.

Unless specially indicated, either sodium hydroxide or potassium hydroxide should be used as alkalis.

Solutions of ferric chloride, silver nitrate, and other reagents and indicators, that are added in quantities measured by a few drops, should be kept in droppers, preferably with pipettes. Bottles containing other solutions for general use in the laboratory should also be provided with pipettes (better graduated pipettes) capped with rubber teats. The pipette should pass the bore in the plug and almost reach the bottom of the container.

Other materials that will be necessary in the laboratory are distilled water (kept in a large bottle provided with a tubulure, or with a siphon tube with a clip), drying agents (calcium chloride, sulphates of sodium, calcium and magnesium, potash, soda lime, caustic alkali, etc.; see Experiment 3), active carbon, lumps of pumice or brick for boiling liquids during distillation (Experiment 4), filter paper, test papers (litmus, congo, universal indicator), cotton and glass wool, and soft copper wire.

Snow and ice are also often required in the laboratory. Snow (ice) should be mixed with water since air that is present between particles is insulator of heat and the cooling process will be retarded. A cooling mixture consisting of table salt and three parts (by weight) of snow or ice is sometimes used in the laboratory. Some processes, e.g. diazotization, require pure ice or snow. Common salt (edible or technical) can be used to salt out substances from their aqueous solutions.

There should be mixtures for washing laboratory glassware. They should be kept by side of the sink. If the glassware is heavily contaminated with substances that fail to be removed with water or common solvents, chromic-sulphuric acid should be used. This is a mixture of 10 g of potassium dichromate in 40-50 ml of warm water and 200-250 ml of concentrated sulphuric acid. As the acid is slowly added to the dichromate solution with stirring, much heat is liberated. Allow the mixture to cool and place it in a dry bottle provided with a glass stopper. Keep the bottle in a flat-bottomed glass or porcelain dish. The chromic-sulphuric acid wettens glass well and removes organic contaminants from its surfaces. Washing will be more effective with slightly heating the mixture. Spent solution should be returned into the bottle. Never discard it into the sink. When the washing mixture turns green, discard it and prepare a new portion. If sodium dichromate is used instead of potassium dichromate, dissolve 10 g in 10-15 ml of water. Chromic-sulphuric acid is hygroscopic. If kept in a bottle closed with a damaged stopper, it will absorb atmospheric moisture: its volume will increase, and the acid will flow over the bottle neck.

A warm 15 per cent solution of trisodium phosphate, especially one containing pumice or brick in powder form, is also a good washing liquid, but it fails to remove resinous substances. Commercial detergents may also be used for the purpose.

When any solution is discarded into the sink, the tap should be open to the full so that ample water dilutes the aggressive liquids.

Spent solutions containing silver or iodine, and also organic solvents, should be collected in special containers and recovered by distillation (the solvents). Spent organic solvents can also be used for washing glassware from organic contaminants. The laboratory should have also special bins to collect paper, filters, and other wastes that cannot be put into the sink. Residues of metallic sodium should be kept in a bottle filled with anhydrous paraffin.

The laboratory should have a special cabinet containing drugs and bandaging materials that may be needed to render first medical aid in cuts, burns, etc., two or three pairs of goggles that will be used in some experiments, and one or two pairs of rubber gloves that should be used to remove accidentally spilt acids or alkalis (see Chapter 2). Finally, the laboratory must be provided with boxes with dry sand and shovels, a wool blanket (to cover the victim if his clothes take on fire), and also fire extinguishers (see also Chapter 2).

CHAPTER TWO

LABORATORY ROUTINE. SAFETY

Methodological Hints to Instructor

It is recommended that the work in the laboratory should continue not less than three or four hours at a time. The author thinks that two-hour sessions are less effective. Longer studies help the student to plan his work more efficiently and ensure better possibilities for his independent work. The significance of the latter fact is difficult to overestimate.

An experienced assistant or an instructor should be present in the laboratory to guide the students in their exercises. The instructor should see to it that the students do not smoke or take food in the laboratory. Loud talking is not allowed either since it distracts the student.

Before the laboratory work, the student must prepare himself theoretically at home. He must be aware of the subject of the nearest laboratory job and the experiments, so that he could read the corresponding material in his textbook or lecture records. The programme of laboratory experiments should be posted in the laboratory in the table form. It is reasonable that the instructor had a brief talk with each student so that he might be aware of the student's preparedness to the experiment. The instructor should minimize, or even avoid at all his instructions to the students immediately before the work.

The student should perform all operations in the laboratory as independently as possible. It is desirable that the work should incorporate the elements of investigation rather than thoughtless performance of the prescribed manipulations. It is useful therefore to give the student an unknown substance, or a mixture, so that he could not foresee the results of the determination of physical constants or elemental qualitative analysis of the given organic substance (in Experiments 7-17). It is also useful to give students samples of one substance bearing different labels (sample numbers).

If the result of the experiment is not satisfactory, the student must repeat the procedure with the same or another substance.

The students do not need petty guardianship, but general supervision. To check the student knowledge in the subject, it is sufficient to have a talk with some individuals or with the whole group. A talk can reveal the knowledge of the theory too. It is also desirable that the instructor should look through the students' records in their notebooks from time to time and make the corresponding corrections wherever necessary. This will obviate the necessity for a student to fill in questionaries and compile special reports. Our vast experience shows that the questionaries that are usually included in foreign manuals (the American manuals in particular) are harmful rather than useful, since they offer the student a standard series of questions and do not help him develop independent way of keeping his records.

Programmed control is also useful in everyday work. It can be realized in the form of brief questions relating to the theory, and student's brief answers written on a separate sheet of paper which the student signs and indicates the date and the number of the question. It is recommended that the programmed control should be in a way constructive so that the student could give an unassisted answer instead of selecting the right answer from a series of answers suggested in the ticket. The selection of the proper answer from a number of suggested ones facilitates the control on the part of the instructor, but it burdens the student's memory with wrong formulations and only checks the student's ability to make the right choice rather than his true knowledge.

It is convenient to make special notes not only in the instructor's notebook but also in posters that will show completion by the student of each laboratory job. This poster will clearly illustrate the work of each student and the group on the whole, and will help the instructor plan his control of the students' work. This system has been developed in the laboratory headed by the author and it proved quite effective.

Instructions to the Student

General Notes. The methods of work, and the apparatus used in the laboratory of organic chemistry differ significantly from those used in laboratories of inorganic and analytical chemistry. Many organic substances are non-electrolytes and the rate of the reaction between them is therefore slower than that of ionic reactions. If the prescribed conditions for a given reaction are for some reason altered or modified, the reaction can be accompanied by side or secondary reactions. The resultant product can thus be a mixture of substances strongly differing in their properties.

It is therefore recommended to follow strictly all specifications of the procedure, such as the ratio of the reactants, the process temperature and duration, etc.; it is also necessary to use special apparatus and devices, and to be able to purify the obtained substance.

Since many organic substances are sparingly soluble in water, other solvents (often volatile and inflammable) should be used. Special care should be taken in handling these substances. Each student should acquaint himself with the laboratory regulations and how to render first aid to himself and his mates in accidents.

Preparing for work. Before starting the laboratory work, the student must learn the theory concerning the subject of the experiment. Next he should read attentively the description of the laboratory job in this manual so that he could clearly understand the object of the experiment and its procedure, and be ready to answer the instructor's questions.

The student must obtain, and prepare for work, all necessary apparatus and reagents.

Stoppers and tubes. Cork stoppers should be treated thoroughly on a cork press before use. Holes in them can be made with a dry cork borer. In boring rubber stoppers a drop of glycerol or alkali solution should be applied onto the borer. The bored stopper should be washed immediately. Cork stoppers can be bored only after treating on a cork press. Bored stoppers should not be pressed. Boring should be done in two steps: first on the narrow end of the stopper, to half its depth, and then on the wider side. This prevents formation of rugged edges at points where the borer would otherwise appear.

After a long use, rubber stopper can be destroyed by many organic liquids (e.g. hydrocarbons, aldehydes, etc.) or their vapours, and tar the reagent. Glass or cork stoppers should be used in such cases.

In order to cut a glass tube, a notch is first made with a file, the tube is then held in two hands, the thumbs pressing against the notch, and the tube is then resolutely broken. To cut a wide or thick-walled tube, a notch is first made, and a drop of molten glass is applied onto the notch (low-melting milk glass strips, taken from broken thermometers, suit the purpose). A transverse crack appears on the tube at the point of application of the molten glass. As other glass drops are placed at the ends of the developing crack, the tube is cut by its circumference. Sharp edges of the cut tube should be filed or fused over a burner. This prevents hand cutting and strengthens the tube edges (fusing).

In order to bend a narrow glass tube, it is first heated strongly and uniformly over a length of 6-8 cm. The tube should be held over the burner in both hands and turned along the axis. A flat flame burner should preferably be used for the purpose, but if such is not available, the tube can be held in the flame of a common burner in an inclined position and moved there and back with constantly turning it along the axis over the required length. The softened

tube should be removed from the flame, and its ends moved gently upwards until the required angle is attained. The bent tube should then be fixed with its hot section in the air and allowed to cool.

A special blowpipe is required to bend large diameter glass tubes (see Chapter 1).

Assembling Apparatus. Before assembling any apparatus read attentively this and the previous chapter. The apparatus should be assembled very carefully, without undue haste, taking special care as not to break its separate components. Plugs and separate joints should be prepared before fixing the apparatus on the stand. Glass parts should be wrapped in strips of paper or asbestos before they are fixed in metal clamps of the stand (unless the clamps are lined with rubber or cork). Test tubes and flasks provided with side arms should be clamped in the stand at points above the soldered joint.

Glass tubes, adapters, and thermometers should be passed through cork or rubber plugs and only then inserted into the flask neck, test tube, or tubulure. Substances that rapidly destroy cork or rubber are seldom used in this course of practical chemistry. The glass part to be inserted into the cork or rubber plug should first be lubricated with a drop of water or glycerol, then held firmly with the fingers as close to the point of insertion as possible, and put into the hole with gently turning the glass part around the axis. The stopper and the part should then be wiped dry.

If there is a small difference in diameters of separate parts to be joined together (e.g. a test tube and an adapter) it is convenient to replace the stopper with a length of soft rubber tube (better red or yellow rubber). To increase the thickness of a rubber tube, roll it, or use two or three pieces of glass tubes of different diameters so that they could be tightly passed one into another.

If a part of the apparatus enters the other part relatively tightly, the joint can be sealed with a piece of rubber tubing (Fig. 8). This type of joint is easy to assemble and disassemble. It is especially convenient because it is not rigid and the joined parts can swing slightly in relation to one another. The area of rubber exposed to the action of organic liquids or vapours is insignificant too.

Before joining glass parts with rubber they should also be lubricated to decrease friction, and held close to the point of connection.

Wherever possible, liquids should not accumulate in the joints and contact rubber tubings or stoppers. For this reason all joints should be made so that their upper members are narrower than the lower, and enter the latter to the length of 1-3 cm below the plug or tubing ends. When fixed on a stand, the clamp should grip the apparatus at the point *below* the joint, and paper or asbestos should be placed between the glass and the clamp.

In some cases, where it is necessary to release excess pressure in the apparatus, or to read the thermometer at the point where it passes through the stopper, part of the latter is removed as shown

in Figs. 3 and 17. No apparatus shall be run unless it is communicated with the atmosphere through a vent, or through a cut in the stopper (in the coldest part of the apparatus).

A sketch of the assembled apparatus should be drawn in the notebook.

Other General Operations. Wherever possible, all starting substances and the resultant products should be weighed (even in cases where the yield of product is not calculated). Solids should be weighed on a watch glass or a sheet of glossy paper, and liquids in test tubes or flasks. The weight of the container or paper (watch glass) should be known.

To weigh a test tube or a round-bottom flask, they are hanged from the hook (over the left pan) of the balance by a soft wire which is bound round the vessel (either filled or empty) at its mouth.

In distillation it is convenient to weigh the empty test tube intended to collect the distillate and the vessel from which the liquid is distilled. The vessels should be tied up with fine wires and weighed before and after distillation to determine the weight of the distilled fraction and the residue by difference of weights (see Experiments 4 and 5). Liquids the density of which is known should be measured by volume (see Chapter 1).

To prevent mistakes in carrying out parallel experiments with different substances, the test tubes or other containers should be labelled with a glass-writing pencil or with a common pencil on a strip of paper glued on the glass. It should be remembered that if a container is long kept on a hot water bath (or some other heater) the marks of a glass-writing pencil can be destroyed. The mass of containers should also be marked directly on the glass. As a rule there is a ground spot on glass containers. If it is absent, it can easily be made using a fine abrasive paper. All data of the experiments (container No., its contents, weights of containers and substances, etc.) should also be put into the notebook.

Carrying Out Experiment. During the experiment, the bench should be kept in order and cleanliness. No extraneous objects are allowed on the bench. The absence of order and carelessness are often the cause of wrong results and sometimes even accidents. For this reason, while preparing the experiment, the student should put away from the bench all unnecessary objects, such as various utensils, strips of paper, tubes, stoppers, etc., and the bench itself should be wiped dry.

Some experiments should be carried out in a hood. In each particular case this will be specially indicated.

Once begun, the experiment should be continued to the end without haste, with conscious performance of each step. If a doubt arises, it is better to consult the instructor or the laboratory assistant rather than your mate.

All observed phenomena should immediately be put down in the notebook (whenever possible). The results of the experiments should also be written down immediately. On the termination of the experiment (or a series of experiments) the apparatus should be allowed to cool, then disassembled, all glassware emptied (except containers that hold substances needed for further experiments) and washed thoroughly with water from the tap, with organic solvents, or with special mixtures (see Chapter 1), depending on the nature of the contaminants.

The apparatus should be disassembled and its separate parts washed after removing the plugs and rubber parts, that can otherwise be affected with aggressive detergents. The washed parts should be rinsed with water from the tap, then with distilled water, and dried on pegs in the overturned position. To accelerate drying, the glassware can be held over a flame of the burner and blown with air through a tube inserted into the vessel. A pump, bellows, a rubber syringe, or an aspirator (see Chapter 1) can be used for the purpose. Rinsing glassware with small quantities of alcohol significantly accelerates drying. The washings should not be discarded. Various fans (even those used for hair drying) can be used as well.

Keeping Records. The student must keep full records of the processes for preparing the experiment, the procedure, and the experimental results. He must write down the date, the object of the experiment, names (numbers) of substances used, conditions and particulars of the procedure, names and quantities of the reagents, and especially the phenomena observed during the experiment, even those that may appear insignificant at first sight. All calculations, reaction equations, and the results of the experiment should also be carefully put down into the notebook. The book should have margins for special notes, remarks, etc. It is better to put all major records only on the right page of the notebook leaving the left one for calculations and notes. Calculations, such as multiplication or division (except the simplest one) can be done with a four-place table of logarithms or a slide rule, provided the accuracy to the third significant figure is sufficient.

The student must formulate the results and put them down into the notebook.

If the object of the job is a parallel study of various substances, the results should be better presented in the form of a table, to make them more illustrative.

The text of the manual should not be transferred word to word into the notebook. The student must learn how to formulate himself, saving no time or paper in this case.

It is not recommended to make records by memory (at the end of the laboratory work), or make preliminary records on occasional clips of paper, and then re-write into the notebook. While carrying

out experiments, the student not only learns the corresponding material, but acquires habits for future investigation as well. A true researcher must not rely upon his memory, but must keep detailed record of the work done.

If, by chance, the student puts in his notebook an erroneous statement or wrong results, they should not be deleted but only crossed out so that in case of necessity they could be read. A special note should then be put on the margin.

The notebook is a report of the student on the work done in the laboratory. For this reason, the student must re-read his records and make the corresponding corrections, if any.

Prevention of Accidents and First Aid

All experiments offered in the present book are quite safe provided all instructions are scrupulously followed. Nevertheless, each student must be well acquainted with the safety rules and be ready to render first medical aid to himself and his mates in accidents.

Sodium metal, bromine, acids, and inflammable organic solvents (benzene, benzine, etc.) should not be kept in the laboratory in large quantities. Residual quantities of metallic sodium should not be discarded into the sink, but collected in special bottles containing liquid paraffin.

Handle smaller vessels with solutions and substances holding the entire vessel in your hand (rather than the neck). Hold large bottles by their necks and carry them on the palm of the other hand.

Heat test tubes and other glass containers very carefully and gradually. See to it that before putting the vessel over a naked flame or on a gauze, it should be wiped dry.

Do not lean over the reaction vessel or look at its content through the neck. When heating any liquid, direct the vessel mouth away from yourself and your mates in the laboratory. Wear goggles when heating concentrated acids or alkalis.

Handle ether, benzene, lower alcohols, acetone, and other inflammable liquids away from the open flame, and try not to inhale their vapour. Heat them only on baths with closed heater elements. If an inflammable liquid takes flame inside a vessel, close it tightly with a glass plate, porcelain or metallic object, or a wet towel, or even with a wooden plate: the flame will thus be extinguished. Never try to blow off the flame or extinguish it with water. If the burning liquid is spilt on the floor extinguish the flame with dry sand from the box using a shovel which must be available in any laboratory. If the fire is in the hood, first close the shutter or the door and then proceed as instructed above.

If a fire happens in the laboratory, turn off all burners and electric heaters and use fire extinguishers to control incipient fires. Fire extinguishers should be regularly checked.

Use a woolen blanket to fight fire on a man. Wrap the victim tightly and hold for 1-2 minutes. This time is sufficient to extinguish flame.

Treat slight burns with glycerol or with cotton wool soaked in alcohol. In stronger burns, place cotton wool or gauze soaked in saturated aqueous solution of picric acid or 1-2 per cent potassium permanganate, or tannin solution. This will remove the pain and prevent vesication. Next treat the affected site with Vaseline. Do not wet the burned skin with water. If the pain is strong, give the victim a tablet of aspirin before carrying him to the doctor.

Many organic compounds, such as phenyl hydrazine, aniline, nitro compounds, aromatic hydrocarbons, and other noxious substances are harmful to the respiratory ducts, the skin and the whole body. All substances in the organic laboratory should therefore be handled with special care trying not to inhale their vapours. If some substances get on the hands, they should be washed thoroughly with soap and a brush.

When liquid bromine gets on the skin, the clothes, or on the bench, treat the site immediately with concentrated (20-40 per cent) solution of sodium thiosulphate and then wash off with ample water. Treat the skin with Vaseline.

If acid or alkali gets on the skin or clothes, wash them immediately with ample water, and then with a 3 per cent solution of sodium bicarbonate (for acid) or 1 per cent acetic acid (for alkali). If the burn is severe, apply then a pad of cotton wool and gauze soaked with solutions used for heat burns.

If the eye is affected, wash it with ample water, then with a 2 per cent $NaHCO_3$ solution (for acid) or saturated boric acid solution (for alkali). Wash the eye for at least fifteen minutes, and then consult a doctor. Keep solutions for treating the eyes in the medical cabinet in droppers with pipettes or in small washers provided with beaks.

If the skin is injured with broken glass, remove its fragments with forceps, treat the wound with rivanol (1 : 500) and apply a bandage. Fasten it with adhesive tape. If noxious gas is inhaled (bromine, chlorine, etc.), go to fresh air. It is also useful to breathe in a weak solution of ammonia.

The safety instruction, and also the means to fight incipient fires and to render first medical aid should be hanged in a conspicuous and easy-to-get place. A wall-mounted cabinet should contain all necessary medicines, solutions, small scissors, bandaging and other materials that may be needed in accidents. Each accident, even very slight, should be reported to the instructor, and a doctor consulted in each case.

CHAPTER THREE

PURIFICATION OF ORGANIC COMPOUNDS. DETERMINATION OF THEIR MAJOR CONSTANTS. QUALITATIVE ANALYSIS

Experiments given in this chapter acquaint the student with the general methods of work with organic substances. These methods will then be often used in other experiments. Especially important are the methods of isolation and purification of substances, since the reactions, in which organic substances are formed, are often accompanied by side reactions and the substance in question is contaminated with various impurities.

Each of the described experiments can be carried out with various materials, and the substances specified in individual experiments should be given preference only because of their availability or convenience in use

1
Crystallization

REAGENTS

Benzoic or *oxalic acid.*

Place 1 g of benzoic acid and 50 ml of water in a beaker or a flask of 75-100 ml capacity, and heat the mixture to boiling. Benzoic acid dissolves completely. Pass the hot solution quickly through a small pleated filter and divide into two parts. Quickly cool one part by immersing the vessel in cold water: benzoic acid precipitates in the form of fine needles. Allow the other part of the hot solution to cool for 20-25 minutes: benzoic acid precipitates in the form of large scales.

If oxalic acid is used, dissolve 2 g of the acid in 5 ml of water in a test tube with heating, filter the solution, divide it into two parts and cool at different rates as instructed above. Oxalic acid crystallizes in the form of needles. Like in the former case, the size of crystals depends on the rate of cooling.

Separate benzoic (or oxalic) acid crystals by filtration with suction on a small round piece of filter paper in a funnel with a perforated disc (see below). Without interrupting suction, press the crystals with a flat glass stopper. Discontinue suction, wash the precipitate with a few drops of cold water, suck again, transfer onto a strip of filter paper, and dry.

Re-crystallized and dried benzoic acid can be used for determinating the melting point (see Experiment 7).

As a contaminated substance is dissolved and re-crystallized, the impurities remain in solution. Insoluble impurities can easily be separated by filtering the hot solution. Drops of water-insoluble liquid impurities, such as oils or resins, can be separated by passing the aqueous solution through a filter paper wetted with water.

To decolourize stained solutions, add a small quantity of active wood or animal charcoal, heat, and filter. Add charcoal into a cold or warm solution. To avoid vigorous foaming, do not add charcoal into hot solutions.

It is easy to purify a substance by crystallization if its solubility in a given solvent differs significantly at low and high temperatures. For example, the solubility of benzoic acid, $C_7H_6O_2$, at 18 °C is 2.7 g and at 100 °C 59 g in 1000 ml of water, i.e. one part by weight in 370 volumes and in 17 volumes of the solvent respectively. The solubility of oxalic acid, $C_2H_2O_4 \cdot 2H_2O$ (see Experiment 74), at 20 °C is 140 g, and at 100 °C, over 1100 g in 1000 ml of water. Substances that dissolve well in the cold should be crystallized with gradual evaporation of the solvent.

The proper choice of a suitable solvent is of decisive importance in purifying substances by crystallization. In dubious cases, the solvent should be selected after preliminary tests with small quantities of the substance.

Substances with non-polar and low-polarity molecules better dissolve in non-polar solvents. And vice versa, the substances whose molecules are polar, or those having the ionic structure, better dissolve in polar solvents. To summarize, the closer the chemical nature of substances, the better they dissolve one another.

If commonly used solvents are arranged in the order of their gradually decreasing polarity, the series will be as this: water—methyl alcohol—ethyl alcohol—ethyl acetate—acetone—ethyl ether—chloroform—benzene—carbon tetrachloride—ligroin (benzine). A substance soluble in two solvents that do not stand one after another in the series usually dissolves in all other solvents standing between the two. All these liquids are quite volatile and therefore do not contaminate crystals after drying.

The selected solvent should either dissolve the impurities well or not dissolve them at all; it should not react with the substance

to be purified either. During re-crystallization, part of the substance is usually lost with impurities.

Small crystals are usually obtained on rapid cooling and large crystals on slow cooling of solutions. The appearance of large crystals of many substances is characteristic, but sometimes such crystals incorporate droplets of the mother solution. On the other hand, fine crystals, whose total surface area is larger than that of large crystals, sometimes adsorb much impurities from the solution. The purer the substance, the better it crystallizes.

Sometimes crystalline substances are separated from solution first as oil; to initiate crystallization, a seed crystal of the same substance should be dropped into the liquid.

It is more convenient to separate crystals from the mother liquor by filtering with suction. To do so, separate large quantities (10-20 g

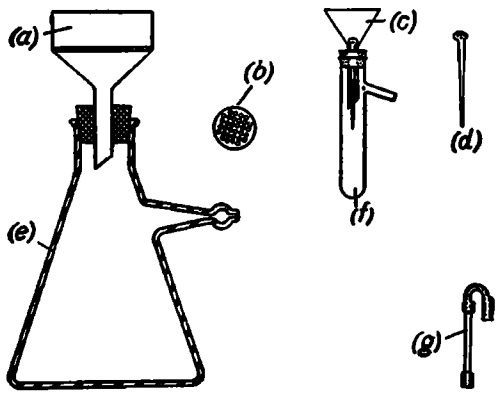


Fig. 6. Apparatus for filtering with suction

and over) of crystals on a Buchner funnel (Fig. 6*a*). Place a round piece of filter paper on the funnel bottom. The diameter of the paper should be slightly smaller than the bottom diameter. A common glass funnel may also be used: a perforated porcelain disc should then be placed in the funnel (Fig. 6*b*). The filter paper diameter should be slightly larger than of the disc.

It is convenient to separate small quantities of crystalline precipitate using a funnel with a Willstatter nail (Fig. 6*c* and *d*). To manufacture the nail, take a glass rod that freely passes the funnel stem and is 2-3 cm longer than the stem. Strongly heat one of its ends in the flame of a burner. Flatten the softened glass, pressing the rod end against a metallic or porcelain surface. The diameter of the head thus made should be a few millimeters larger than the section of the funnel stem. Fuse the other end of the glass rod.

If the hot glass rod is flattened against a rough surface, such as that of a coarse file, the obtained grooves will facilitate drying of precipitates by suction.

Place the nail inside the funnel and close with a round piece of filter paper, whose diameter is 4-5mm larger than that of the nail head. Pass the funnel stem through a plug or a piece of rubber tubing, and instal the funnel into the vessel for suction—a thick-walled conical flask (Fig. 6*e*) or a test tube (flask) with a side arm (Fig. 6*f*). This vessel will collect the mother liquor or washings. Connect the vessel to the suction pump (mechanical or hand operated) or to an aspirator (see Chapter 1) using a thick-walled rubber tubing and a guard tube.

To begin filtration, wet the filter paper in the funnel with the solvent used in the experiment and press the paper tightly to the perforated disc and the funnel walls. Hold the filter paper in place with a glass rod and pour the solution on the rod. Transfer the crystals using the same rod or a spatula. Apply vacuum gradually. When the mother liquor has been sucked off, stop the vacuum pump, and wet the crystals on the filter with a small portion of the same solvent. Switch on the pump again and continue suction for a few minutes until the liquid stops dripping.

Remove the funnel from the vessel, place it upside down on a sheet of filter paper, and discharge the filter with the precipitate by tapping the funnel walls against the table. If a perforated disc was used, it can be pushed out using a glass rod. The nail protrudes from the funnel stem and can also be easily removed by pushing down the protruding end. Remove the crystals from the paper and the funnel walls, and dry the precipitate on the filter paper sheet.

If a hot saturated solution is filtered into a thin-walled flask or a test tube, first place 1 or 2 ml of pure solvent into it and heat to boiling so that the rising vapour warms up the funnel (without filter): the solution will not then crystallize in the funnel. If the solution is filtered into a thick-walled receptacle, heat the funnel separately before filtration. It is also recommended to shorten the funnel stem.

In some cases, especially if the mother liquor and the washings are then discarded, it is convenient to suck the liquid straight from the vessel (beaker, test tube). To do so, immerse a narrow glass tube with a small funnel at the end, packed with a dense cotton pad or wet filter paper (Fig. 6*g*), into the solution and connect the upper end of the tube to the suction vessel. Remove the liquid through the tube, press the crystals with the tube end, add little solvent to wash the crystals, mix, and suck off the liquid again. Now transfer the crystals onto a sheet of filter paper and dry. The method is inapplicable for small quantities of crystalline precipitates.

2
Crystallization from Mixed Solvent

REAGENTS

Acetanilide (see Experiment 207).
Ethyl alcohol, rectified.

Place 1 g of acetanilide and 5 ml of ethyl alcohol into a test tube. Heat and shake the test tube on a hot water bath until the mixture begins boiling. Attain complete dissolution of acetanilide. Transfer one half of the obtained alcoholic solution into another test tube and cool. Add, with shaking, warm water (12-15 ml) to the remaining hot solution until slight turbidity appears, then heat slightly to clarify the solution, and finally allow it to cool.

Crystals are not precipitated from the alcoholic solution of acetanilide, but exquisite shining crystals fill the whole larger volume of the water-alcohol solution on shaking.

The solubility of acetanilide in alcohol is quite significant (one part by weight in four volumes at 20 °C and in one volume at 70 °C), and it does not markedly change with heating. Saturated solutions of acetanilide are too concentrated and significant loss of the dissolved substance is inevitable during filtration (on the walls of the vessel, on the filter, and in the mother liquor). Moreover, the concentration of impurities is much higher in such solutions, and their purification is thus difficult.

Crystallization from a mixture of two solvents is often used in such cases. One solvent should mix with the other but dissolve the precipitated crystals as little as possible.

The solubility of acetanilide in water at 20 °C is about one part by weight in 200 volumes, and at 100 °C in about 20 volumes, i.e. much lower than in alcohol. If water is added to alcohol, the solubility of acetanilide decreases at all temperatures. This phenomenon is used to saturate a hot solution in the experiment. The solution becomes cloudy, and ample crystals precipitate on cooling.

Crystallization from an oversaturated solution can be accelerated by rubbing the vessel wall with a glass rod, or adding a seed crystal.

3
Solvent Extraction

REAGENTS

Hydroquinone.
Ethyl ether.
Sodium benzoate.

A. Place 2 g of hydroquinone and 40 ml of water into a 50-100 ml flask. Heat the mixture in warm water (not over 50 °C) with shaking to complete dissolution, and cool well in cold water. Transfer the solution into a 100-150 ml separatory funnel (Fig. 7*a*), add 10-15 ml ether, close the funnel with a stopper, and turn it upside down,

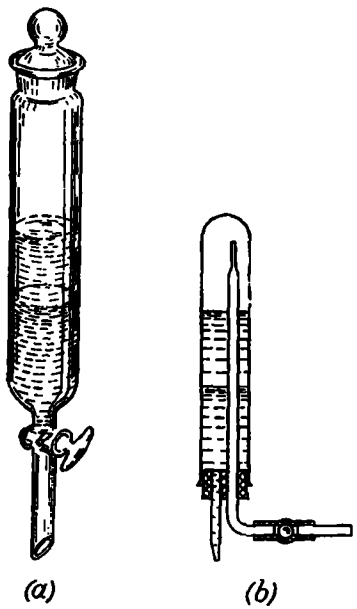


Fig. 7. Apparatus for separation of immiscible liquids

holding the stopper with one hand and the tap with the other. Open the tap for a short while to release the ether vapour, close again, shake vigorously the funnel in the overturned position for a few seconds, and open the tap again. Shake for a longer time, release the ether vapour, turn into the right position, and keep on the stand for a few minutes until the water and the ether layers separate. Now remove the stopper and pass the aqueous layer through the tap into a flask. Close the tap, and pour the ether layer through the mouth into a dry beaker or a dish.

Evaporate carefully the ether extract in a HOOD on a warm water bath (*away from open flame*) to recover the greater part of the original hydroquinone. Press out excess liquid and weigh the hydroquinone.

B. Place 0.3 g of sodium benzoate and 3 ml of water in a test tube, and shake to dissolve the crystals. Add 3-4 drops of concentrated hydrochloric acid to the solution: benzoic acid precipitates. Cool the test tube in water, add 5 ml of ether, close the test tube with a stopper, and shake carefully until the precipitate dissolves. Allow the mixture to stand to separate the layers, and immerse a pipette with a drawn end to the bottom (Fig. 5*a*), closing its upper end with the forefinger. Hold the test tube at the level of the eye. As the pressure of the forefinger on the pipette top is now released, the liquid is slowly filled into the pipette from the lower layer by the action of hydrostatic pressure. As soon as the whole lower layer has filled the pipette, close the pipette top with the finger again, remove it from the test tube and discard the aqueous layer. If the pipette is too narrow, the aqueous layer fails to be fully transferred into it. Then repeat the operation, or suck the liquid carefully by the mouth.

Transfer one half of the remaining ether solution into a dish and evaporate carefully (*away from open flame*). Crystals of benzoic acid extracted by ether remain in the dish.

Add 1 ml of dilute alkali solution to the remaining ether extract. Close the test tube with a stopper and shake strongly several times. Slightly open the stopper from time to time (see above). Allow the mixture to stand, lower the pipette to the bottom again, take in the heavier water-alkali layer, transfer it into a clean test tube, and add a few drops of concentrated hydrochloric acid. Precipitation of benzoic acid indicates that it is extracted, in the form of a salt, from the ether solution with aqueous solution of alkali. The remaining ether layer should be collected in a special bottle.

Solvent extraction is often used to isolate a substance from a solution or a mixture. The following principle underlies the choice of a suitable solvent: the presence, and especially accumulation, in a molecule of hydroxyl, carboxyl, and amino groups, usually increase solubility of a substance in water, while the presence and accumulation of halogen atoms or hydrocarbon radicals increase solubility in ether and in non-polar organic solvents, such as benzene (see explanations to Experiment 1).

Different solubility of a substance in two immiscible solvents is often used in solvent extraction. As the equilibrium is attained (on shaking), the substance in question becomes distributed between the solvents so that the ratio of its concentrations in the upper and the lower layer is equal to a constant value—the ratio of its solubilities in given solvents. This ratio is known as the **distribution coefficient**. It depends on the nature of a given substance, the nature

of the solvents used, and the temperature, but does not depend on the initial concentration of the substance or on the absolute quantities of the substance and the solvents (**Nernst distribution law**).

To ensure more complete extraction of a substance, it is recommended to extract it with smaller portions of the solvent but as many times as possible. The character of distribution becomes more complicate with the changing state of the substance, e.g. its dissociation, or reaction with the solvent.

In Experiment B, the predominant transfer of benzoic acid into the ether or aqueous solution is determined by the state in which it is present: free or in salt form.

Salts of sparingly soluble acids and bases are often well soluble in water. Aqueous alkali is therefore commonly used to extract acids, and dilute hydrochloric or sulphuric acids, to extract bases.

Separatory funnels are used to separate considerable volumes of liquids (Fig. 7*a*) and if the volumes are small, a pipette (Fig. 5*a*) should be used to take the lower layer. An apparatus shown in Fig. 7*b* is often used instead of a pipette. To manufacture the apparatus, bore two holes in a rubber plug and pass into them a short tube, ending at the plug edge level, and a longer tube, reaching almost to the bottom of the test tube. The outer end of the shorter, and the inner end of the longer tubes should be drawn. The outer end of the longer tube should be bent at an angle, and a piece of a rubber tubing with a glass bead inside it should be put on its end. Insert this plug into the test tube containing the liquids to be separated, close the open end of the shorter tube with the finger tip, turn the test tube upside down, and release the finger over a receptacle.

Press the seal and adjust the flow-rate. Discharge the lower and then (into another receptacle) the upper layer.

If a volatile solvent is used (ether, chloroform, etc.), only cooled liquids may be placed in the apparatus, and the vapour should be released from the test tube as often as possible (see above), since when mixed together, the liquids can liberate much heat and develop high vapour pressure. Lubricate the mating surfaces in taps of separatory funnels with Vaseline (see Chapter 1).

The obtained solutions of substances in organic solvents, or liquid substances, should be dehydrated before their distillation or distillation of solvents. Depending on the chemical nature of the liquid, it is dried by various anhydrous substances that readily bind water. Table 1 gives characteristics of commonly used dehydrating agents.

Dehydrating agents should not be used in large quantities. Only 2-3 small lumps will be sufficient. They should be placed into the liquid to be dried and allowed to stand for a few hours (better overnight). Organic liquids containing water are sometimes cloudy. Slight heating with a dehydrating substance accelerates clarification.

Table 1

Dehydrating Substances

Substance	Substances that can be dehydrated	Efficiency
Calcium chloride	Hydrocarbons, halogen derivatives, ethers, and some esters	Medium
Calcium sulphate	Almost all organic substances	Medium
Sodium sulphate	Ditto	Medium
Copper sulphate	Most organic substances, except those forming complexes with copper salts (amines, glycols, etc.)	Low
Magnesium sulphate	Almost all organic substances except those easily dehydrating	High
Potassium carbonate	Alcohols, ketones, amines	Medium
Sodium hydroxide, soda lime, potassium hydroxide	Some hydrocarbons, amines	High
Phosphoric anhydride	Hydrocarbons, halogen derivatives	Very high

Calcium chloride should be used at temperatures not above 30 °C to prevent partial dehydration of the hydrate that is formed. Decant carefully the clear liquid, or pass it through glass wool.

As dehydrating substances absorb moisture they often deliquesce (except sulphates). Spent dehydrating substances (salts) can be recovered by heating in a porcelain (better iron) dish to 200-250 °C with stirring.

4
Distillation

REAGENTS

Any organic liquid boiling at 80-150 °C, such as *benzene*, *toluene*, *butyl* or *isoamyl alcohol*. The liquid should preferably be contaminated with coloured impurities, but free from water (see Experiment 3).

Assemble the simplest apparatus for distillation (Fig. 8). Close the test tube (or a flask) with a plug through which a thermometer is passed. The mercury bulb should be somewhat below the level of the side arm. See to it that the part of the scale reading the anticipated temperature is not concealed from the eye by the stopper. Some 10-15 °C of the scale reading below and above the anticipated temperature should also be seen. See also that the thermometer does not touch the vessel walls. Fix the vessel in a stand at the point above the side arm and connect a 40-45 cm condenser tube (held in another

stand). The condenser diameter should be greater than that of the side arm. Calibrate and mark receptacles into which the distillate will be collected. If low-boiling liquids are distilled, cool the receptacle with water.

Place a few millilitres of liquid and a boiling stone into a test tube (or flask) with a side arm. Liquid should be filled into the test tube through a funnel so that its drops do not get into the side arm. The liquid level should not rise above the point in the midway from the bottom to the side arm. (If distillation is carried out in a flask, the liquid level should not be above the middle of its bulb.) Weigh

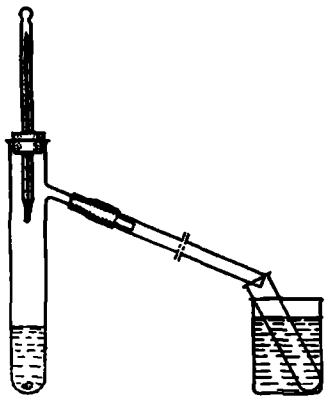


Fig. 8. Distillation with a straight tube condenser

the liquid or measure its volume. Weighing should be done straight in the vessel, the empty weight of which (without a stopper, thermometer, and condenser tube) should first be determined (see Chapter 2).

Close the distillation vessel with the plug bearing the thermometer, put the first receptacle beneath the condenser outlet, and heat carefully the liquid in the vessel over a low flame, rotating the burner in circles under the vessel so that flame does not reach the empty part of the test tube. Boiling must be quiet. Read the thermometer and observe distillate dripping into the receptacle. Record the temperature at which the first drop of the distillate falls into the receptacle. The rate of distillation should be about one drop in 1-2 seconds. See to it that there is always a drop of the distillate hanging from the thermometer bulb. The absence of the drop indicates overheating of the liquid.

Heat the vessel containing an inflammable liquid, such as acetone, hydrocarbons, etc., on a gauze (see Experiment 10). Do not heat it over a naked flame.

If the mercury column of the thermometer sets, after distillation of the first drop, at the level close to the anticipated temperature (for corrections see Experiment 10), almost all distillate is collected in the first receptacle (within the range of 1-3 °C). If the liquid contains considerable quantities of volatile impurities, the distillate, boiling out at a temperature below the actual boiling point of the main substance, is collected in the first receptacle, and the main part of the distillate, that boils out within a narrow temperature range, in the second one. In some cases it is convenient to collect the fraction boiling at higher temperatures into the third receptacle, like in fractionation (see Experiment 5).

At the end of the distillation process, wipe dry the receptacles on the outside (if they were cooled in water) and weigh them. Allow the distillation vessel to cool slightly, remove the plug with the thermometer and the condenser, wipe the vessel containing residual quantities of the substance (to remove soot), and weigh too. Record the results of weighings in the notebook and calculate percentage content of each fraction, and also of non-distilled residue in the starting material.

If a substance is pure, all, or almost all its volume is distilled within the range of 1-2 °C. Substances contaminated with volatile substances, or impurities that decompose on heating, are distilled in a wider temperature range. Since many organic substances are hygroscopic or decompose in storage, the first portions of the distillate (even of a dried substance) are cloudy and contain traces of water or other impurities. If the distilled substance is further used in synthesis, or for determination of physical constants or elemental composition (Experiments 7-17), the first portion of the distillate is collected separately, and only the main fraction is used for further experiments. This rule concerns all substances, even those boiling out in a narrow temperature range.

Sometimes it is not necessary to control accurately the vapour temperature during distillation. The still is then closed with a plug without thermometer (Fig. 14).

During boiling and distillation, the liquid can bump because of local overheating, and even splash out of the vessel. To prevent this, it is recommended to place into the liquid, before heating, pieces of porous material (such as pumice, brick, broken pottery) having the size of a wheat grain, or glass capillaries soldered at the upper end. Bubbles of air issuing from the pores facilitate the formation of vapour in the depth of the liquid and ensure quiet boiling.

If after a prolonged boiling, or after an interruption in the process, the liquid bumps, add a fresh boiling stone. The hot liquid can vigorously foam, and it should therefore be first cooled. Overheating, which sometimes occurs in the absence of air in the liquid, can be

considerable. For example, water can be heated under atmospheric pressure up to 137 °C without apparent boiling.

If the distillation vessel (especially a test tube) is heated above the liquid level, the local overheating of vapour can distort the results of the experiment.

In distillation of volatile substances boiling out at temperatures below 70-80 °C, it is expedient to collect the distillate into test tubes with tubulures, using the 'cold finger' type condenser (Fig. 3*d*), or a water-cooled condenser. On the contrary, during distillation of high-boiling liquids (b.p. over 200 °C), and especially of substances solidifying on cooling, do not use any condenser but collect the distillate directly from the side arm of the distillation vessel. It is convenient to distil high-boiling substances from test tubes and flasks provided with side arms located as low as possible. Discard used stones to waste (Chapter 1).

Distillation and crystallization are the operations that are most frequently used in isolation and purification of organic substances. Distillation is as a rule possible in cases where the boiling points of the substance and its impurities differ significantly. Distillation with a thermometer makes it possible to judge on the purity of a substance (see Experiment 5) and on the boiling point of the pure substance, its major physical constant (see Experiment 10).

During distillation of high-boiling substances it is necessary to take into account the error of the thermometer reading arising from cooling of the mercury column in the region above the vapour level (Experiment 10).

Substances that do not distil without decomposition under atmospheric pressure are often purified by distillation in vacuum, i.e. with evacuation of air from the distillation vessel. This significantly decreases the boiling point. If the pressure decreases two times, the boiling point decreases 14-20 °C, i.e. under residual pressure of 10-20 mm Hg the boiling point is usually 80-120 °C below that under atmospheric pressure.

5
Fractionation

REAGENTS

Xylene (or *turpentine fraction* boiling at 152-157 °C).
Carbon tetrachloride (or *chloroform*).

Use a mixture of equal parts by weight of carbon tetrachloride, CCl_4 (b.p. 77 °C, density 1.59 g/cc), and xylene, C_8H_{10} (b.p. 139 °C, density 0.86 g/cc). This mixture (density 1.12 g/cc) is convenient in that respect that its components have distinctly different boiling

points and densities. Therefore, it is easy not only to determine, to a high degree of accuracy, the composition of the distilled fractions by their density, but also to follow the changes in their composition in repeated distillation.

Carry out fractionation from a 75-100 ml flask with a side arm to which a water-cooled condenser is connected (Fig. 9). Close the flask with a plug through which a thermometer is passed. See to it that the part of the scale reading from 65 to 160 °C is open to the

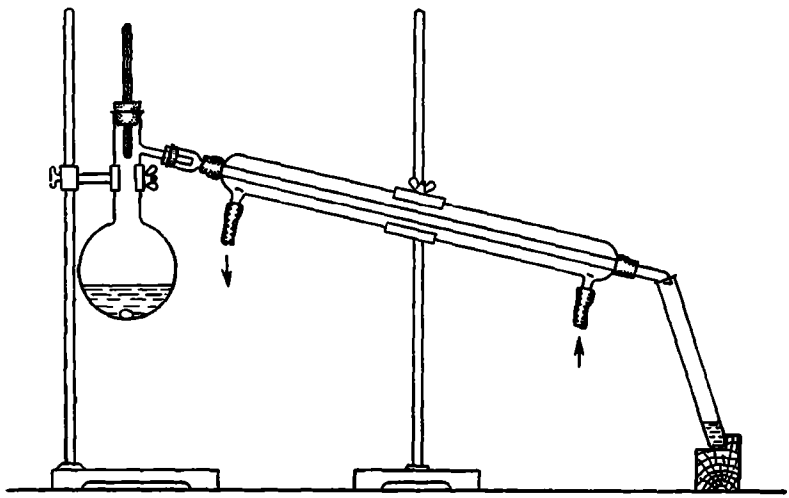


Fig. 9. Fractionation still with a water-cooled condenser

eye. Before beginning the process, prepare six dry narrow test tubes that will be used as receptacles. They should be provided with wire loops for convenience of weighing, and labelled as follows: *1*, *1a*, *2*, *3*, *4*, and *4a*. Weigh each test tube to an accuracy of 0.1 g and put the results in the notebook.

A. Place 25 g (22.5 ml) of the starting mixture into a fractionating still taking special care that no liquid gets into the side arm. Add a boiling stone and close the flask with the thermometer. Put test tube *1* to the condenser outlet, and heat the flask carefully over a small flame (see Experiment 4).

Change the receptacles to collect three fractions boiling out within the following temperature ranges: *1*, to 95 °C; *2*, from 95 to 110 °C; and *3*, from 110 to 125 °C. When the temperature of the rising vapour is 125 °C, discontinue heating, allow the flask to cool slightly, and transfer the remaining liquid into the fourth test tube (*4*, from 125 to 139 °C).

Mark the liquid level in each test tube, weigh them, and record the mass of each fraction.

B. During the second distillation, aimed at isolation of pure components, fractions *1* and *4* are separated into narrower fractions and the distillates are collected within the following temperature ranges: *1*, to 82 °C; *1a*, from 82 to 95 °C; *2*, from 95 to 110 °C; *3*, from 110 to 125 °C; *4*, from 125 to 132 °C; and *4a* (still residue), from 132 to 139 °C.

Transfer fraction *1* (of the first fractionation) into the empty distillation flask, and collect, in the same test tube, the fraction boiling out at temperatures below 82 °C. Discontinue heating, allow the flask to cool slightly (1-2 min), then add fraction *2* of the first fractionation, and heat again to collect the fraction boiling at temperatures below 82 °C in the same test tube *1*. Continue heating and collect the fraction boiling out within the temperature range from 82 to 95 °C in test tube *1a*. Discontinue heating at a temperature 95 °C, add the first fraction *3*, and collect the new portions of the distillate in the corresponding ranges of temperatures into test tubes *1a* and *2*. (As a rule, no distillate is added to test tube *1* in this case.) As soon as a temperature of 110 °C is attained, add the last fraction (*4*) of the first fractionation to the still residue and collect the distillate in test tubes *2* (a few drops), *3*, and *4*. Discontinue heating at 132 °C and transfer the cooled residue into test tube *4a*.

Using a glass-writing pencil (of a different colour) mark the new level on each test tube, and weigh them to determine the mass of each fraction obtained in the second fractionation.

C. To assess qualitatively the efficiency of fractionation as the method of separating mixtures, compare the odour and other properties of the extreme fractions of the second distillation (*1* and *4a*). Place a drop of each fraction in two different test tubes containing water. The drop of fraction *1* sinks to the bottom, while the drop of fraction *4a* floats on the water surface. Place a drop of each fraction onto a glass plate and try to light them up. Fraction *1* (CCl_4) does not burn, while fraction *4a* (C_8H_{10}) produces a smoky flame.

D. Record the results of the qualitative tests in the notebook, transfer all fractions from the test tubes into special bottles, and fill water from a burette into each test tube to the mark. The volume of each fraction can thus be determined to an accuracy of 0.1 ml. Once the mass and the volume of each fraction are known, it is possible to calculate their densities (to an accuracy of the second decimal place); using the graph given in Fig. 10, determine the percentage composition of each fraction. Put the weight and composition of each fraction into the notebook and determine their variations in the first and the second fractionations. The differences are especially vivid when presented graphically as in Fig. 11. Each fraction in the diagram is represented in the form of a column the height

of which is proportional to the mass of the given fraction. Each column has two parts, viz., open and shaded, their size being proportional to the contents of each component in the fraction. For the sake of convenience, percentage content of one component can be written down over each column.

In the described experiment, carbon tetrachloride can be replaced by chloroform (b.p. 61 °C, density 1.49 g/cc). A mixture of equal parts by weight of chloroform and xylene has a density of 1.09 g/cc

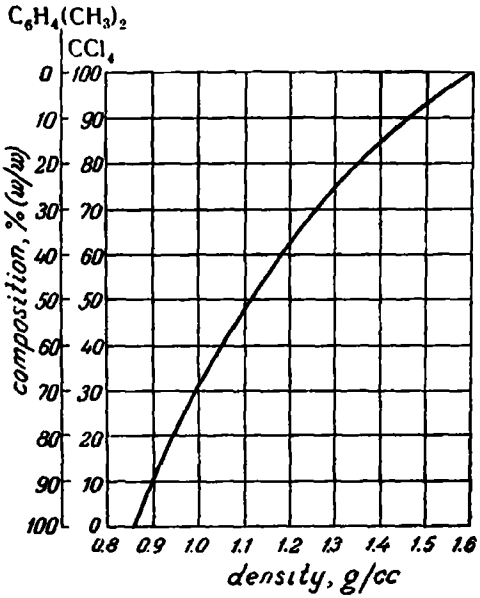


Fig. 10. Density of xylene and carbon tetrachloride mixtures

The dependence of density of this mixture on its composition is described by the curve shown in Fig. 12.

The procedure with this mixture is the same as described above. Since the difference in boiling points of the mixture components is greater, it is recommended, during the first fraction, to collect five (not four) fractions boiling out within the following temperature ranges: *1*, to 78 °C; *1a*, from 78 to 95 °C; *2*, from 95 to 110 °C; *3*, from 110 to 125 °C; and *4* (residue), from 125 to 139 °C. During the second fractionation, the following fractions are collected: *1*, to 70 °C; *1a*, from 70 to 95 °C; *2*, from 95 to 110 °C; *3*, from 110 to 125 °C; *4* from 125 to 132 °C; and *4a* (still residue), from 132 to 139 °C.

A pinene fraction of turpentine (152-157 °C) can be used instead of xylene in both mixtures (with $CHCl_3$ and CCl_4). This fraction makes a considerable part of technical turpentine. Pinene has a density of 0.86 g/cc, which is almost the same as of xylene, and the

same graphs (Figs. 10 and 12) can be used to determine the composition of the fractions by density. The boiling point of pinene is 155-156 °C, and as mixtures containing pinene are fractionated,

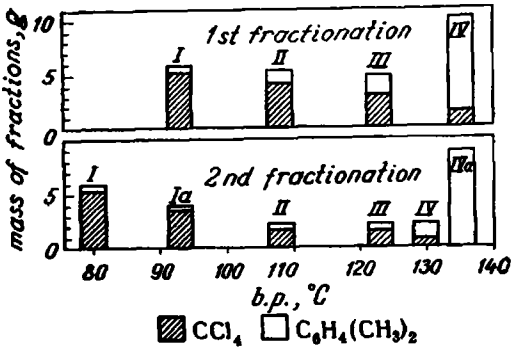


Fig. 11. Fractionation of a binary mixture

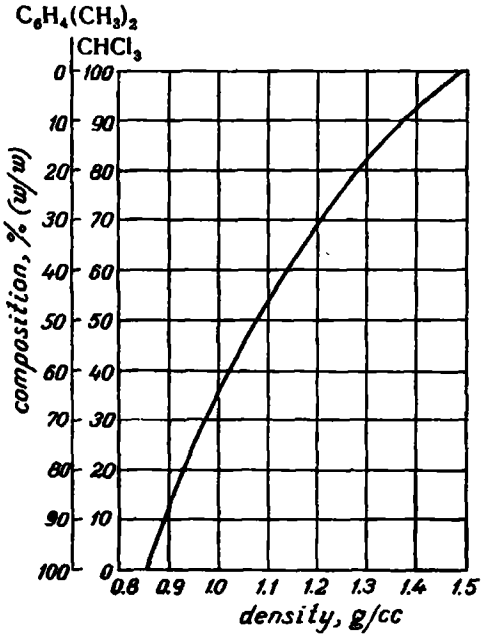


Fig. 12. Density of xylene and chloroform mixtures

pinene is concentrated in the residue after distillation of the fraction boiling out at temperatures below 150 °C.

The theory of distillation of mixtures has been worked out in detail by D.P. Konovalov. The vapour composition of most binary mixtures (i.e. those consisting of two components), boiling at any

temperature under constant pressure, is characterized by the increased content of a more volatile component compared with its content in the liquid phase. For this reason, during fractionation of such mixtures, the more volatile component is concentrated in the first fractions, and the less volatile constituent in the last fractions or in the still residue. If fractionation is repeated several times and the temperature ranges of the extreme fractions are narrowed, with subsequent fractionation of the intermediate fractions, the mixture components can practically be fully separated from one another.

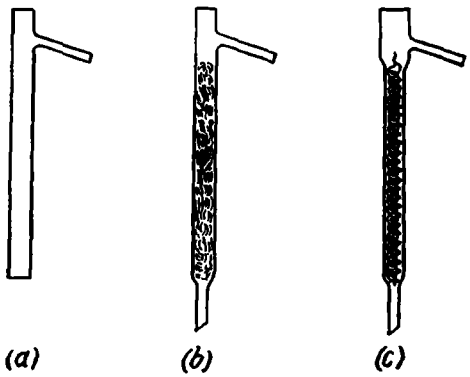


Fig. 13. Partial condensers

The fractionation becomes more effective and rapid if partial condensers (fractionating columns) are used. The rising vapour is partially condensed before it enters a straight-run condenser, and the distilled part of the mixture thus becomes richer in the low-boiling constituent.

Dephlegmators (partial condensers) of various design can be used in the experiments. The simplest, and least effective one, is shown in Fig. 13*a*. This is a straight tube with a side arm in its upper portion. The height of the tube is 150-200 mm, the diameter 8-12 mm. The efficiency of this apparatus can be improved if a loose pack of glass wool is placed inside (Fig. 13*b*); as the vapour passes through the condensate films, its low-boiling components are retained in them. The apparatus can be made even more effective by placing, inside the glass tube, two nichrome spirals. Spirals can be made by winding the wires round two glass rods of different diameters; the obtained spirals are then placed one inside the other. The spiral ends should be twisted together (Fig. 13*c*). Condensate films are especially readily formed on the spirals and the liquid flows back into the still. Metal spirals are inapplicable for distillation of acid solutions.

If the vapour does not rise to the level of the side arm, wrap the dephlegmator with asbestos or some other incombustible material and fix it with wire. This insulation will improve the operation of the dephlegmator by preventing its uneven cooling with the environing air. For the same reason, it is recommended to wrap the dephlegmator with heat-insulation material or to put a wider glass tube (on cork spacers) on it when low-boiling substances are distilled. The annular gap between the tubes should be about 5-10 mm. The upper part of the dephlegmator and the side arm should also be well wrapped. If the distillation rate is slow, even the simplest dephlegmator (Fig. 13*a*) will give satisfactory results with such insulation.

The experiments offered in this book will not require more complicate dephlegmators.

In some cases a binary mixture (at a certain ratio of its constituents) is distilled like a simple substance (*azeotropic mixture*) at a constant temperature, which is either higher or lower than the boiling points of its pure constituents. Such mixtures fail to be fractionated by common distillation, because the composition of the liquid and that of the vapour are the same.

Here are a few examples of such mixtures (parenthesized are the weight ratio of the components, and the boiling point at atmospheric pressure): ethyl alcohol-benzene (32 : 68, 68 °C), ethyl alcohol-ethyl acetate (30 : 70, 72 °C), ethyl alcohol-chloroform (7 : 93, 59 °C), ethyl alcohol-carbon tetrachloride (16 : 84, 65 °C), chloroform-acetone (80 : 20, 65 °C), acetic acid-toluene (28 : 72, 105 °C). Water also forms azeotropic mixtures with many organic solvents, e.g. with ethyl alcohol (5 : 95, 78 °C), isoamyl alcohol (50 : 50, 95 °C), ethyl ether (1 : 99, 34 °C), chloroform (3 : 97, 56 °C), benzene (9 : 91, 63 °C), toluene (20 : 80, 84 °C), ethyl acetate (8 : 92, 70 °C), and dichloroethane (20 : 80, 72 °C). First distilled portions of liquids that sparingly dissolve water are often cloudy. This is explained not only by distillation of water (see the next experiment), but also by the formation of azeotropic mixtures. Distilled alcohol and ether often require dehydration for the same reason (see Chapters 6 and 19). The phenomenon of formation of azeotropic mixtures is often used for removal of water by distilling it with some other solvent, e.g. with toluene. Low-boiling ternary azeotropic mixtures, such as water-ethyl alcohol-benzene (8 : 18 : 74, 65 °C) are especially convenient for the purpose. During distillation, nitric and hydrochloric acids also produce azeotropic mixtures with water.

The composition of boiling mixtures depends on the pressure under which the distillation is effected.

If the composition of a binary mixture differs from that of azeotropic, part of the component that is present in excess (with respect

to the azeotropic mixture) can be isolated by fractionation. To separate components of an azeotropic mixture, it is necessary to bind one of its constituents chemically.

6
Steam Distillation

REAGENTS

Aniline.

(See also Experiment 202.)

Place 1 ml of aniline, 8 ml of water, and a boiling stone into a wide test tube. Stopper the test tube with a plug through which a wide bent tubing is passed. Fix the test tube in the stand, and put the end of the outlet tube into another test tube that will serve as a receptacle. Immerse the receptacle in cold water as shown in Fig. 14.

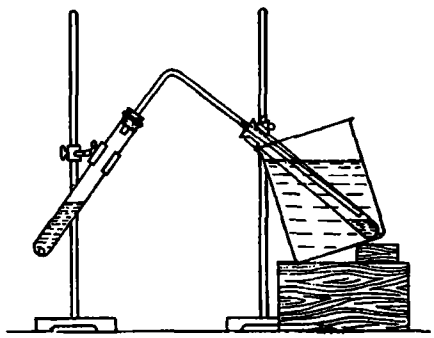


Fig. 14. Distillation from a test tube

Heat the test tube contents carefully over a burner until they boil. Boiling should be quiet. The rising vapour is condensed in the bent tube and on the walls of the receptacle. Discontinue distillation when about two-thirds of the original volume of the liquid are collected in the receptacle. The last portions of the distillate should drip in clear (not cloudy) drops.

The milky distillate is an aqueous emulsion of aniline. Large drops of aniline quickly separate from the distillate and form an oily layer. The ratio of aniline to water in the distillate is about 1 : 4 or 1 : 5.

The residue in the test tube contains so little aniline that it cannot be isolated on cooling even as turbidity. It follows that despite the high boiling point (184 °C) aniline quickly and almost completely passes into the receptacle together with water at a temperature of about 100 °C. The aniline layer in the receptacle is almost colour-

less, even if the starting material was stored for a long time and turned brown. Hence the coloured impurities remain in the distillation vessel and do not pass into the receptacle.

Steam distillation is often used to separate substances that are sparingly soluble in water, the vapour pressure of which at 100 °C is appreciable (5-10 mm Hg or over). The vapour pressure of water and that of a substance immiscible with water grow with temperature independently, and distillation commences when the summary vapour pressure is equal to atmospheric.

Such a mixture is thus distilled at a constant temperature that is somewhat lower than the boiling point of pure water, and water vapour and the vapour of the substance in question (A) are condensed simultaneously in the condenser. Their weight ratio in the distillate (m_A/m_{H_2O}) is equal to the ratio of products of the vapour pressures p_A and p_{H_2O} (at the temperature of distillation) and their molecular masses:

$$\frac{m_A}{m_{H_2O}} = \frac{p_A \cdot M_A}{p_{H_2O} \cdot 18}$$

It follows that steam distillation of any substance immiscible with water is easier and faster at higher vapour pressure of this substance at the temperature of distillation, and at higher molecular mass. The formula also shows that the quantity of the substance in the original mixture does not matter.

Steam distillation can be used to isolate from mixtures and to purify many substances boiling at very high temperatures, or even decomposing at temperatures of distillation.

If large quantities of substances are to be distilled, a special steam generator should be used. Steam is delivered through a tube into the mixture containing the substance in question and the mixture of vapours thus formed is then condensed. Superheated steam is used to distil substances boiling at especially high temperatures.

The molecular weight of aniline, $C_6H_5NH_2$, is 93. Its solubility in water is not high (3 per cent at 20 °C and 6 per cent at 100 °C). The boiling point is 184 °C; the vapour pressure at temperatures of about 100 °C is of the order of 50 mm Hg. Hence, during steam distillation of aniline, the share of water vapour pressure is about 710 mm Hg.

The approximate weight ratio of aniline to water in the distillate is

$$\frac{m_A}{m_{H_2O}} = \frac{50 \times 93}{710 \times 18} \approx \frac{1}{3}$$

It follows that if the original mixture contains about 1 g of aniline (density 1.02 g/cc), it can be distilled with the first 3 ml of water. In reality this formula does not hold quite exactly because aniline

is appreciably soluble in water, especially with heating, and because the aniline molecule contains the hydrating amino group.

The vapour pressure of resinous impurities, contained in aniline, is very small and they are not therefore distilled with water vapour.

7
Determining Melting Point

REAGENTS

A pure substance melting at 40-150 °C, e.g. *naphthalene*, *diphenylamine*, *diphenyl*, *benzoic acid*.

Wash thoroughly a low-melting glass tube in distilled water and dry. Put on the goggles and heat the glass tube in its middle part over a burner until it softens. Remove the tube from the flame and draw in the vertical direction to obtain a long thin-wall tube, 1-2 mm in diameter. Cool the tube and cut into 10-12 cm lengths. Solder the tubes at both ends and keep in a box. Before the experiment, cut them in twos. (If the capillaries are stored with open ends, moisture can condense inside them.)

Dry the substance in question and grind it thoroughly. Take a small portion of the substance with the open end of the capillary and transfer it to the sealed end by slightly tapping. To pack the powder in the capillary, use a thin glass rod or a wire. The powder can also be compacted by energetically tapping the capillary against a glass surface. The column of compact powder should be 3-5 mm high.

Attach the capillary to a thermometer using a rubber ringlet (a narrow piece of tubing) or a spiral of soft wire (Fig. 15*a*). The substance column must be at the middle of the mercury bulb. Fix the thermometer with the capillary (or several capillaries) in a dry and clean test tube using a stopper with a cutout on the side of the thermometer scale (Fig. 17*a*). The thermometer should not touch the test tube walls, and its bulb should be 0.5-1 cm above the test tube bottom. Fix the test tube in the vertical position in the stand and immerse into liquid in a beaker (or a flask) supported on a gauze. The liquid level in the beaker should be above the mercury bulb in the test tube, and the test tube itself should be at least 0.5-1 cm above the beaker (flask) bottom (Fig. 15).

The test tube holding the thermometer can also be fixed straight in the neck of the flask (in a stopper) containing liquid. A test tube having a wider upper part, or provided with lateral lugs, which would prevent it from sinking into the flask neck, can also be used.

Heat the assembled apparatus slowly on the gauze over a small flame with stirring at short intervals, using a stirrer or the test tube

with the thermometer, and watch the thermometer readings and the state of the test substance in the capillary.

Adequate illumination is required.

If the substance is unknown, raise the temperature at a rate of 10-12 °C per minute, and obtain tentative results. Now repeat the experiment (after cooling the apparatus) and raise the temperature first at a faster rate, and then (at a temperature some 10-20 °C below

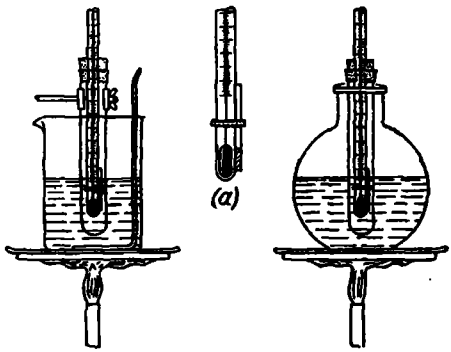


Fig. 15. Melting point apparatus:
— thermometer bulb with a capillary end

the anticipated melting point) slow down the heating rate to 1-3 °C per minute.

Observe and record all changes in the state of the test substance: change of colour, decomposition, agglutination, sintering, etc. When the substance shrinks markedly and begins liquefying, remove the burner. The beginning of melting is marked by appearance of the first liquid drop in the capillary. The end of melting is disappearance of the last crystals.

The melting point, i.e. the temperature corresponding to the equilibrium between the solid and the liquid phase, is a very important characteristic (constant) of a solid substance. It can be used to identify an organic substance, i.e. to establish its likeness to a known substance (see below). The melting point is the characteristic of substance purity: if a substance melts at a temperature below its true melting point, or its transition from the solid to the liquid state is indistinct, this indicates the presence of impurities.

Usually a pure substance melts within a narrow range of temperatures measured by 0.5-1 °C, even if the substance is partly decomposed by heating. But carbohydrates, salts of acids and amines, and also amino acids often melt (with decomposition) within a wider range of temperatures. Some substances are decomposed, charred, or volatilized without melting. The melting point is then sometimes determined in a sealed capillary, or the temperature of decomposition is determined.

Most organic substances melt or decompose at temperatures below 300-350 °C. At high melting temperatures a correction should be introduced for the part of the mercury column that is cooled (Experiment 10). This correction usually does not exceed 2-3 °C.

In the described apparatus, the thermometer and the capillary containing the test substance are present in an air bath and are out of contact with the heated liquid. This is more convenient than frequent measurements of temperature by immersing the thermometer and the capillary into the liquid. The liquid in the beaker is stirred with a glass or wire stirrer made in the form of a ring provided with a handle.

If the melting point of a substance in question is known to be below 90-95 °C, water should be used as the heating medium. If a substance melts at a higher temperature, concentrated sulphuric acid, colourless mineral oils (Vaseline or paraffin), glycerol, or silicone fluid should be used.

If the working liquid is sulphuric acid, the apparatus can be heated to 240-250 °C, and re-used many times. When the acid darkens, add a small crystal of saltpetre to decolourize it.

A charge of sulphuric acid can be used for 3-4 months; during this time it can absorb much water from the air and its boiling point can decrease to 200 °C and below.

Heat the vessel containing sulphuric acid very carefully. The vessel should first be wiped dry on the outside. WEAR GOGGLES.

Mineral oils or glycerol are less dangerous in accidents from careless handling, but require frequent renewal and can be heated only to 200-220 °C; moreover, their vapours are combustible.

If the capillary is not sufficiently clean, the melting point can be a few degrees lower.

When dealing with unknown substances, it is recommended first to heat carefully a small sample (a few crystals) in a test tube, or in a lid of porcelain crucible, over a flame of the burner (see Experiment 14).

8
Changes in the Melting Point in the Presence of Impurities

REAGENTS

Naphthalene and *diphenylamine*, pure.
Mixture of 80% of naphthalene and 20% of diphenylamine.
Mixture of 80% of diphenylamine and 20% of naphthalene.

Weigh out 0.8 g of one and 0.2 g of the other component and grind them thoroughly in an agate mortar, or first fuse them in a short test tube and then grind into powder.

Other pairs of substances can also be used in the experiment, e.g. naphthalene-phenol, naphthalene-diphenyl, naphthalene-benzoic acid. These pairs are, however, less convenient because phenol is hygroscopic, and produces burns on the skin; diphenyl is relatively expensive; and benzoic acid melts at a temperature above 100 °C, which makes it impossible to use water in the apparatus.

Of mixtures melting above 100 °C, the pairs urea-cinnamic acid and benzoic acid-benzamide are suitable for the given experiment (see also Experiment 9).

Place samples of the two original pure substances, and their two mixtures, each in a separate capillary (see Experiment 7). Attach all the four capillaries to the thermometer sides using a rubber ringlet, and record their position around the thermometer. It is more convenient to arrange them by their increasing length and to record their contents in the same order. The samples in the capillaries should be at the same level, against the middle of the mercury bulb.

Fix the thermometer and the capillaries in the apparatus (Fig. 15) filled with water, and heat carefully. Mark accurately the temperatures at which each sample begins melting and melts completely. Pure substances melt within a very short interval of time and temperatures (0.5-1 °C), while their mixtures, within the range of temperatures measured by 5-10 °C and over.

The obtained data can be presented in the form of a graph. Accordingly, plot the percentage composition of a sample against the axis of abscissas, and the melting temperatures against the axis of ordinates. Use dots to designate pure substances and vertical lines, characterizing the range of temperatures, for mixtures. Draw descending lines to connect the points characterizing the melting point of a pure substance with the upper ends of the nearest vertical lines. Continue the lines to find the approximate point of intersection.

9
Checking Identity of Substances by Melting Point of Mixed Sample

REAGENTS

Urea.
Cinnamic acid.

The substances are ground to fine powder and kept in labelled bottles or test tubes.

Take small (at the tip of a blade) samples of two substances (labelled by different numbers) and prepare three capillaries and the

apparatus for the determination of melting points above 100 °C (see Experiment 7). Place the samples into separate capillaries and determine their melting points. To that end, fix the capillaries on the thermometer, one by side the other, and first heat at a high rate to 110 °C. Then slow down the heating to 1-3 °C per minute. Record the temperatures at which both samples melt (they must be almost the same). Now mix small, approximately equal portions of the substances on a clock glass using a spatula, and place the mixed sample into the third capillary. Meanwhile the apparatus should cool. When the temperature drops to 80-85 °C, remove the thermometer, detach the capillaries, and fasten the third instead.

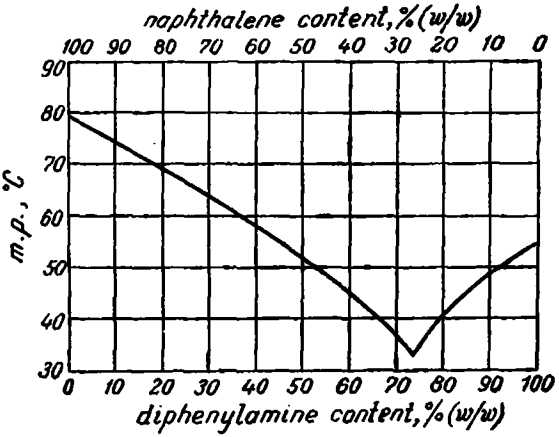


Fig. 16. Phase diagram for naphthalene and diphenylamine mixtures

Determine the melting point of the mixed sample by slowly heating the apparatus. Intently watch the changes that the sample undergoes at various temperatures. Record them. When the sample is completely molten, compare the melting points of the pure substances and their mixture. Derive a conclusion on the identity of the samples.

Even insignificant quantities of soluble impurities (those having higher melting point included) markedly decrease the melting point of substances and widen the range of temperatures within which it melts. Exceptions are quite seldom.

By preparing mixtures in which the components are taken in various proportions, and by plotting their melting points on the graph, it is possible in some cases to construct by this simple method the phase diagram of the system. Figure 16 shows such a diagram for mixtures of naphthalene and diphenylamine. The curve has the lowermost, eutectic, point at 32.5 °C.

The form of the curve indicates whether or not the components in the system react in the molten state, and also the composition and the character of the formed compounds.

This is one out of many physico-chemical methods of analysis used by D. I. Mendeleev, and later developed in detail by N. S. Kurnakov and his followers. The physico-chemical analysis has been very fruitful for both the development of theory and practice in many fields of science.

The dependence of the melting point on the purity of a substance is used in a very important practical method of checking identity of a crystalline substance to a known substance having about the same melting point. The substance under examination and the known substance are mixed in small, approximately equal portions, and the melting points of both components and of the mixed sample determined. If the mixed sample melts at the same temperature as the known substance, the substances can, in the majority of cases, be considered identical.

The melting points of urea and cinnamic acid are practically the same, and this pair of substances is therefore especially convenient for Experiment 9. Pairs of other substances, the melting points of which differ only by a few degrees, can also be used. For example, benzoic acid-β-naphthol, cinnamic acid-benzamide, phthalic anhydride-benzamide, etc.

The temperature drop Δt caused by the presence of small quantities of impurities, in the absence of dissociation, association, or chemical reaction, can be determined from the formula

$$\Delta t = KC/M$$

where K is the *cryoscopic constant* of a solvent, which is numerically equal to the fall of the melting point (in °C) caused by dissolution of 1 mole of a substance in 1000 g of the solvent; C is the concentration of the solute (in g per 1000 g of the solvent); and M is the mass of a mole of the solute.

This dependence is employed for the determination of the molecular mass of a substance by the reduction of the melting point of the solvent as the test substance is added (see Experiment 12).

10
Determining Boiling Point

REAGENTS

A pure substance boiling between 60 and 250 °C, e.g. *chloroform, carbon tetrachloride, benzene, toluene, xylene, naphthalene, acetone; propyl, butyl* or *amyl alcohols.*

A. The boiling point of a substance can be determined by distilling it (see Experiment 4). As the first drop of the distillate falls off the condenser end, the temperature is noted and is assumed to be the point at which boiling begins. A pure substance is all (or almost all) distilled within the range of temperatures measured by 1-2 °C.

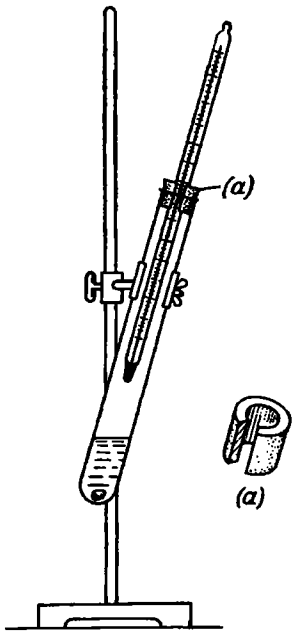


Fig. 17. Determining the boiling point in a test tube:
***a* — split plug with a hole**

The readings of the thermometer would normally require a correction (of the order of 1-2 °C) to compensate for the cooling of the extending column of mercury (see page 63).

B. If a substance is available in small quantity, its boiling point can be determined by a simpler method (though less accurate).

Place 1-3 ml of the substance in question and a boiling stone into a test tube, and close it with a split plug bearing a thermometer. Adjust the height of the thermometer so that its bulb is 4-5 cm above the liquid level and does not touch the test tube walls. Fix the test tube at a slight angle in a stand (Fig. 17) and heat carefully its bottom over a small flame until it boils quietly. To ensure gradual and quiet heating, it is convenient to heat the test tube over a gauze with an asbestos-filled centre having a little hole (the diameter less than that of the test tube) so that the test tube bottom could rest against the edge of the hole. The rising vapour is cooled and conden-

sed on the thermometer and the test tube walls. Heating should be adjusted so that the visible condensate ring is slightly above the upper edge of the thermometer bulb, and the condensate drops fall off the thermometer end incessantly, but at a rate not exceeding a drop in 2-3 seconds. As this demand is met, the mercury column sets constant.

Record the thermometer reading, discontinue heating, allow the mercury column to fall some 10-20 °C, and repeat the experiment to check correctness of the obtained result. The correction should be introduced in this case too. As a rule it would not exceed 1-2 °C.

The boiling point (i.e. the temperature at which the vapour pressure of a substance is equal to the atmospheric pressure), like the melting point, is an important constant of a substance. The boiling point, and also the range of temperatures within which the substance is distilled characterize the purity of a substance and can be used for its identification.

The boiling point depends on the molecular mass, the composition, and structure of a substance. In a series of substances that are similar with respect to their composition and structure, the boiling point usually rises with growing molecular mass. If the halogen or oxygen atoms are substituted in a molecule for the hydrogen atom, the new substance boils at a higher temperature. This becomes especially marked if free hydroxyl or carboxyl groups, which are responsible for the association of particles, are introduced into the molecule.

If a correction, Δt, for the cooling of the thermometer mercury column should be introduced into the result in determining the boiling or melting point of a substance, determine the mean temperature of the glass case of the thermometer at the moment of reading. Accordingly, hold tightly the bulb of another thermometer against the middle of the extending part of the first thermometer column for about a minute. Calculate the difference of both readings $(t_1 - t_2)$, and multiply by the length of the exposed part of the mercury column n (in degrees of the thermometer scale) and by the linear expansion factor of mercury* $\alpha = 0.00016$:

$$\Delta t = \alpha n (t_1 - t_2)$$

Example. The melting (boiling) point of a substance, as determined in the experiment, is 190 °C; the liquid level in the melting point apparatus (or the upper edge of the side arm of the distillation flask in the determination of the boiling point) reads the mark '30' on the

* The factor 0.00016 accounts for the heat expansion of glass. It is used for calculations with engraved-stem thermometers; factor 0.0002 should be used for enclosed-scale thermometers.

thermometer scale. Hence the length of the exposed part of the mercury column is 190 — 30 = 160 °C. If the additional thermometer reads 65 °C at the level of '110' (i.e. 190 — 160 : 2) the difference of temperatures $t_1 - t_2$ is 190 — 65 = 125 °C, and the correction Δt, as found from the above formula, will be

$$\Delta t = \alpha n (t_1 - t_2) = 0.00016 \cdot 160 \cdot 125 = 3.2 \approx 3\ ^\circ C$$

The corrected temperature at which the substance melts (boils) is 190 + 3 = 193 °C. Normal fluctuations of the atmospheric pressure (730-770 mm Hg) usually do not affect the melting point, and produce only insignificant effect on the boiling point.

11
Determining Density of Liquid

REAGENTS

Pure organic liquids (*benzene, chloroform, aniline*, etc.).

Use a 1-2 ml pyknometer, manufactured from a glass tube (Fig. 18*a*). It must be provided with wires for hanging from a balance.

A. *Determining the water number of a pyknometer.* The pyknometer should be washed thoroughly with chromic-sulphuric acid, with water, then dried, and weighed on an analytical balance.

Pour distilled water in a dish or a crucible. Put a soft rubber tube with a glass end-piece onto the wider end of the pyknometer, lower

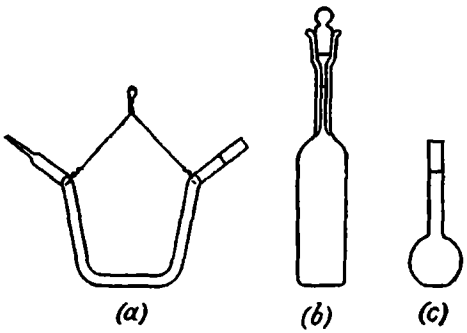


Fig. 18. Pyknometers

its drawn end into the water, and suck it in by the mouth to the level slightly above the annular mark on the wider end. Now remove the rubber tube and immerse the pyknometer in water in a bath (beaker, dish), hanging by the wire from a stand clamp. The temperature of water should be 20 °C, and its level in the bath should be 1-2 cm below the pyknometer ends. In order to maintain constancy

of the temperature in the bath, the quantity of water in it should be not less than 0.5-1 litre. Whenever necessary add warm or cold water to adjust the temperature at the required level. Stir the water thoroughly after adding each new portion.

In 15-20 minutes, adjust the liquid level in the pyknometer accurately to the mark. To do so, touch its drawn end with a piece of filter paper. Now remove the pyknometer from the bath, wipe it thoroughly on the outside (holding by the wire or the wider end), and weigh.

Remove water from the pyknometer, rinse several times with alcohol, dry in a stream of warm air, cool, and weigh again.

The difference in masses of the pyknometer filled with water and of the empty one (filled with air) divided by 0.9970 is known as the **water number** of a pyknometer N. The water number is a constant value for a given pyknometer.

B. *Determining density of a substance.* Fill a clean and dry pyknometer with the test liquid as has been described for filling with water in Experiment A. All other operations are also similar. At the end of the procedure wash the pyknometer thoroughly and dry. The difference in masses of the empty pyknometer and one filled with the test substance at 20 °C is the mass of the test substance m in the pyknometer.

The density of a substance can be calculated from the formula

$$d_4^{20} = m/N + 0.0012$$

Example

The mass of the pyknometer filled with water is 5.5052 g.
The mass of the pyknometer filled with air is 3.5021 g.

The water number is

$$N = \frac{5.5052 - 3.5021}{0.9970} = 2.0091$$

The mass of the pyknometer filled with the test substance is 5.2595 g.
The mass of the substance in the pyknometer, in g, is

$$m = 5.2595 - 3.5021 = 1.7574$$

The density of the substance is

$$d_4^{20} = 1.7574 : 2.0091 + 0.0012 = 0.8759$$

Density is the unit mass expressed in kg/cu·m, or g/cc. It is designated by the letter ρ. Density is a physical constant characteristic of a substance. It slightly changes with temperature, and for this reason the temperature at which the density of a substance is meas-

ured (usually at 15 or 20 °C) is often indicated. The density of a substance is often expressed as relative density d, which is actually the ratio of density of a given substance to the density of a standard substance (ρ_0), i.e. $d = \rho/\rho_0$. Water, the density of which at 4 °C (to be more exact, 3.98 °C) is the greatest (0.99997, i.e. practically 1 g/cc), is normally used as the standard substance. The ratio of the density of a substance at 20 °C to the density of water at 4 °C, d_4^{20}, practically is the same as the density of a substance at 20 °C in g/cc.

The density of water at 20 °C is 0.9982 g/cc, and the value 0.9970 (see above) is the difference of the density of water and density of air (0.0012 g/cc at 20 °C). A correction for density of air should be introduced in both cases: in calculating N and d, since weighing is done in air, not in vacuum. The water number of the pyknometer N is numerically equal to its inner capacity in cubic centimetres, or to the mass of water in this volume at 4 °C, in g.

Normally hydrocarbons are lighter than water. The introduction of double and triple bonds, and also of benzene rings, increases density. The density grows even more if the halogens (especially iodine and bromine) and oxygen (especially —COOH and —OH groups) are introduced into the molecule of a substance. In a homologous series of hydrocarbons, primary alcohols, amines, ethers, and aldehydes, the density grows with the length of the carbon chain. On the contrary, for bromine- and iodine-substituted hydrocarbons, monobasic acids and their esters density decreases with growing length of the carbon chain.

Most liquid organic compounds are lighter than water. All bromine- and iodine derivatives of hydrocarbons, chlorine- and nitro-substituted aromatic hydrocarbons, di- and trichloro-substituted hydrocarbons of the fatty series, formic and acetic acids, and most compounds with several functional groups are heavier than water.

A pyknometer similar to that described above can be manufactured in the laboratory from a glass tube, 4-5 mm diameter, drawn into a capillary at one end and bent as shown in the figure. The ring mark on the wider end should be made with a file. The accuracy of measuring density by the described method is about 0.0002. Pyknometers shown in Fig. 18*b* are also often used. Their capacity is greater and this increases the accuracy of determinations. The disadvantage is that they are more difficult to fill and wash. A very simple pyknometer can be made out of a thick-walled glass tube, diameter 4-6 mm; the tube should be sealed on one end, the bottom blown and flattened, and an annular mark made on the narrow part (Fig. 18*c*). The capacity of such a pyknometer is 0.5-2 ml.

Only approximate values of density (to an accuracy of the second decimal place) can be obtained with an ordinary hydrometer. Moreover, considerable amounts (100 ml and over) of the test liquids are required.

12
Determining Molecular Mass by Lowering Melting Point of Camphor

REAGENTS

Camphor, pure.
Naphthalene, pure.

The reagents should be kept in the powder form in narrow test tubes with stoppers.

Carry out the experiment in an apparatus for determining the melting point (Fig. 15) filled with sulphuric acid, glycerol, or mineral oil.

Weigh accurately 30-50 mg of naphthalene and about 0.4-0.6 g of camphor into a short, absolutely clean, calibrated test tube. Fuse carefully the substances, holding the tube for a short period of time over a small flame of the burner; remove the test tube from the flame and stir the obtained liquid using a stiff wire flattened on one end. Scrape down camphor sublimed on the test tube walls (if any) and mix the contents. Allow the melt to set and remove its greater part onto a watch glass using the same wire.

Grind the mass, load it into a capillary for the determination of the melting point (Experiments 7 and 8) and make a 2-4 mm high compact layer. A wider capillary (about 2 mm) should be used in the experiment. Keep the remaining melt since it may be required to repeat the experiment in case of failure. Fill pure camphor into another capillary.

Attach both capillaries to a thermometer, heat slowly, and watch the changes in the samples (better use a magnifying glass). The melt of camphor and naphthalene begins sintering at a temperature of about 120-140 °C. Slow down the heating and watch carefully to detect the point when the last crystals in the lower layer of the melt, that becomes transluscent, disappear. Record the temperature at this point and assume it to be the melting point of the mixture. Now continue heating and determine the melting point of pure camphor in the other capillary. Another pair of capillaries can be used for control.

The molecular mass M of the test substance is calculated from the obtained data:

$$M = \frac{40 \times 1000 \times m}{m_c (t_c - t_{mix})}$$

where m is the mass of the test substance (naphthalene); m_c is the mass of camphor; t_c is the melting point of pure camphor; and t_{mix} is the melting point of the mixture (camphor and naphthalene). (See also Experiments 8 and 9.)

The value 40 in the formula is the cryoscopic constant or the molecular depression constant of camphor, i.e. lowering of camphor melting point, in °C, caused by 1 mole of solute in 1000 g of camphor.

The formula contains the difference of relatively close temperatures (not their absolute values); the correction for cooling the mercury column of the thermometer should not therefore be introduced.

Camphor has an exceptionally high cryoscopic constant (40). For benzene the constant is only 5.2, and for water 1.9. For this reason it is very convenient to use camphor as solvent: the lowering of the melting point is quite significant and can easily be read off from a common thermometer. Moreover, camphor dissolves well many organic substances. Both of these properties account for a wide use of said method for determining the molecular mass. Its error lies within ±5-7 per cent. The method was proposed by Rast in 1922.

After preliminary checking, other substances can also be used in the experiment instead of naphthalene.

13
Determining Molecular Mass by Vapour Density

REAGENTS

Pure organic substances boiling from 50 to 85 °C, such as *butyl chloride*, *isobutyl chloride*, *tert-butyl chloride*, *chloroform*, *carbon tetrachloride*, *dichloroethane*, *2,2-dichloropropane*, *methyl alcohol*, *ethyl alcohol* (*rectified*), *isopropyl alcohol*, *tert-butyl alcohol*, *ethyl formiate*, *ethyl* (*or methyl*) *acetate*, *acetone*, *hexane*, *benzene*, etc., or mixtures of substances having close boiling points (*petroleum ether*, *light distilled benzine*, etc.).

Carry out the experiment in a volumetric or a common flask having the capacity of 250-300 ml, with a narrow neck closed with a cork plug. Pass a short glass tube, having the diameter of 2-3 mm, through the plug so that its lower end is at the level of the plug lower edge. The upper end of the tube should be drawn into a short capillary above the plug. A wide beaker (better a metallic one) containing hot water and provided with a thermometer should be used to heat the flask. The beaker height should be sufficient to accept the flask to the plug level. Since the flask tends to float on the surface of water in the beaker, hold it immersed in water by limiting its upward motion by a special flask holder, which is actually an aluminium or copper wire, coiled in a ring in its lower part (to hold the flask) and bent in the vertical plane in its upper part for convenient fixing in the stand clamp. The length of the vertical rod of the holder

should approximately be equal to the flask height. The ring is put on the flask from its top to rest on the bulb and thus prevents the flask from floating in water. It is recommended to wrap the beaker (especially a metallic one) with asbestos or other incombustible material and fix the insulation with a wire. The bottom should be left free from asbestos.

Take a clean and dry flask. Close it with a stopper provided with a tube, weigh to an accuracy of 0.01-0.05 g (mass m_1) on a chemical balance. Now immerse the flask in water in the beaker. The temperature of water should be not less than 96 °C. Heat the beaker over a burner or an electric hotplate so that water temperature should not appreciably fall during the experiment. Put the flask holder ring on the flask wider part and fix the upper end of the holder in the stand so that the beaker is immersed in water to the level of the stopper lower edge. See to it also that the flask does not touch the bottom or the walls of the beaker. The bulb of the thermometer should be at the level of the middle of the flask bulb.

Keep the flask in water at this temperature for 5-7 minutes, remove the stopper, add quickly about 2.5-3 ml of the test substance using a short pipette with a wide orifice (without lifting the flask), and close the flask with the stopper again. Do not measure out the volume of the test liquid accurately. As the liquid gets into the hot flask it begins vapourizing. Its heavy vapour displaces the air from the flask and fills it. (The whole volume of the flask is filled, since the liquid is taken in excess.) A small drop is usually first condensed in the plug capillary. It disappears in about 0.5-1 minute; this indicates that the entire substance is evaporated. If a less volatile substance is used, the drop can remain in the capillary. If so, wait until bubbling through this drop discontinues. Do not stop heating the flask, or lower the flame, so that the vapour pressure inside the flask remains constant. Boiling water alone can be added into the beaker if the level drops significantly.

Record the temperature at which evaporation is completed (t); now remove the flask and cool it in running water. Wipe the flask dry with a towel, and weigh again. A portion of vapour can condense and some air penetrate into the flask through the capillary. The new mass is m_2. The difference of masses $m_2 - m_1 = m$ is the mass of vapour of the substance in the volume of the flask at a temperature t. The mass of the drop in the capillary may be disregarded.

Now place the flask in the beaker again and heat for 5-7 minutes. The liquid in the flask is all vapourized during this time. Add a new portion of the same substance and repeat the determination (evaporation, recording of the temperature, cooling, and weighing). Record the data of the first and the second experiment into the notebook and calculate the molecular mass of the substance for each experiment separately. The volume of the flask can easily be

determined after the experiment by filling it with water to the stopper level and then pouring this water into a measuring cylinder. If a volumetric flask is used in the experiment, its full volume can be determined as follows. Measure the diameter and the height of the flask neck from the mark to the stopper edge, and calculate the volume of the cylinder to an accuracy of 1 ml. Add the obtained volume to the known volume of the calibrated part of the flask. The volume of the tube with the capillary can be disregarded in either case.

When calculating the volume of vapour occupying the volume of the flask V at a temperature of water t, it is necessary to calculate as at STP, i.e. to find the volume V_0 from the formula

$$V_0 = \frac{Vp \times 273}{760(273+t)}$$

where p is the atmospheric pressure, in mm Hg, as read off the barometer at the moment of the experiment.

Now use the Avogadro law ($M : m = 22{,}400 : V_0$) to calculate the sought molecular mass:

$$M = m \times 22{,}400 : V_0$$

The described method is a simplified version of the classical Dumas' method for determining molecular masses of volatile substances, developed in the middle of the 19th century. The method gives quite satisfactory results for liquids that boil within the specified temperature range. The vapour pressure of substances that boil at lower temperatures (ethyl ether, ethyl bromide, ethyl nitrite, etc.) is very high at room temperature. As a result, the mass of the cooled flask filled with air and the condensate, and hence the found molecular mass of the substance are very low. For mixtures of substances, the found molecular mass is mean proportional to the mixture components. For example, the molecular mass of benzine boiling at 60-80 °C is of the order of 90-95.

To minimize adsorption of a substance on the stopper, it is recommended to paint the stopper with aluminium lacquer. See to it that the lacquer does not clog the tube opening.

14
Attitude of Organic Substance to Heat

REAGENTS

High-boiling or non-volatile organic substances, such as *sugar*, *glycerol*; *benzoic*, *tartaric*, *citric acids*; *sodium* or *calcium salts of organic acids*, etc.

Place about 0.1-0.2 g of a substance in a small porcelain dish (or into a crucible lid), and heat in a HOOD on a clay triangle or in crucible tongs over a burner. Heating should first be slow, and then the substance can be heated strongly. Observe the changes in the substance: whether or not it melts, volatilizes; check to see that the vapour is inflammable; see if the flame is smoky; see also whether or not water vapour is condensed on a test tube filled with cold water and held above the flame.

If the substance is not fully volatilized, heat stronger until the residue is charred, and ignite it until it becomes white. Cool the dish, add a few drops of water to the residue on ignition, stir with a glass rod, and place a drop on a red litmus paper. If the residue does not dissolve in water, try to dissolve it in hydrochloric acid, adding the acid drop by drop with stirring.

Organic compounds that do not contain metal are normally volatilized or decomposed (charred) on heating, but fully burn on further ignition. The experiment helps establish whether a given substance can boil at atmospheric pressure or melt without decomposition. A smoky flame indicates the high carbon content, i.e. gives grounds for a suggestion that the substance contains multiple bonds, benzene rings, or long carbon chains. Formation of water condensate indicates the presence of hydrogen in the substance molecule (see next experiment).

When strongly heated, salts and salt-like organic compounds containing metals (salts of acids, phenolates, etc.) give non-volatile carbonates of alkali metals (K, Na), or oxides of alkaline-earth metals (Ca, Ba, and also Mg). The ignition products dissolve in water to give alkaline solutions. They are fully soluble in hydrochloric acid. If an insoluble residue is formed, this indicates the presence of heavy metals in the test substance.

15
Detection of Carbon and Hydrogen in Organic Substance

REAGENTS

A dry non-volatile organic substance, such as *sugar*, *naphthalene*, etc.

Copper oxide, powder.

Lime water or *baryta water* (saturated solutions of $Ca(OH)_2$ or $Ba(OH)_2$).

Mix about 0.2-0.3 g of a test substance (liquid or solid) with 1-2 g of copper oxide powder on a clock glass or a piece of paper. Transfer the mixture into a dry test tube provided with a tight stopper

through which a gas tube is passed. Fix the test tube in the stand, almost horizontally, and place the end of the gas outlet tube into another test tube containing 2-3 ml of clear lime or baryta water, so that the gas tube almost touches the liquid surface. Heat the mixture first gently and then strongly.

Observe formation of water drops on the cold walls of the test tube and the gas outlet tube, and also formation of carbon dioxide which becomes apparent from the precipitation of sparingly soluble calcium carbonate (or barium carbonate).

It is not always possible to detect by heating (charring) the presence of carbon in an organic substance, whereas ignition with copper oxide converts all carbon into CO_2 and hydrogen, into H_2O. While oxidizing an organic substance, copper oxide is reduced into metallic copper.

This method is used for both qualitative and quantitative analysis of organic substances.

The test substance should be dried before the experiment to remove hygroscopic water and water of crystallization.

16
Detection of Nitrogen, Sulphur, and Halogens in Organic Substance

REAGENTS

Any organic compound containing said elements, e.g. *aniline*, its *hydrochloride*, *diphenylamine*, *thiourea*, *sulphanilic acid*, *iodoform*.

Sodium metal.

Lead nitrate, 10 per cent aqueous solution.

Sodium nitroprusside, fresh 0.5 per cent solution.

Ferrous sulphate, green vitriol crystals.

Chloroform or *benzene*.

If there are no 'unknown' organic substances (see Chapter 2) containing bromine or iodine, their salts can be added to a solid organic material and mixed well. Chloroform, carbon tetrachloride, picric acid, nitromethane, and other nitro compounds (see explanations to the experiment) should not be given to the student.

Place a few crystals or drops of an unknown substance in a narrow test tube (made out of a 5-6 mm glass tube or used glass ampoule). Hold the test tube in an inclined position and place a freshly cut out piece (the size of a wheat grain) of sodium metal dried with filter paper. The sodium piece should be placed slightly above the substance. Hold the test tube almost horizontally using tongs or a wooden clamp. First heat sodium until it melts. Now set the test tube in the vertical position so that the hot drop falls onto the test sub-

stance. *Take care of the flash.* Heat the mixture to redness. *Stretch the hand to protect the face*, and dip the hot test tube into 5-6 ml of distilled water in a mortar. The test tube breaks down. Carry out this operation behind the glass door of the hood, or wear the goggles.

Grind the black melt with a pestle, transfer the mortar contents into a test tube and heat to boiling. Pass the alkaline liquid through a small pleated filter and use in the tests for sulphur, nitrogen, and halogens. The liquid should be colourless. Yellow or brown colour indicates incomplete decomposition of the original substance. If so, repeat the experiment using a new portion of the same substance.

Test for Sulphur.

A. Add sodium hydroxide solution to 1 ml of lead nitrate solution until lead hydroxide, that precipitates from the first drops, dissolves. Now add a few drops of the alkaline liquid obtained in the experiment (see above).

Development of dark brown colour, or precipitation of black lead sulphide (accelerated with heating) indicates that the test substance contains sulphur.

B. Filter out 1 ml of the alkaline liquid and add 1 or 2 drops of sodium nitroprusside.

In the presence of sulphur the mixture immediately, or gradually, turns bright violet.

Test for Nitrogen.

Divide the alkaline liquid into two parts and add a small crystal of green vitriol to either portion. Boil the mixture for 1-2 minutes, cool, allow to stand for 3-5 minutes, and acidify with dilute hydrochloric acid.

Precipitation of Berlin blue indicates that the original substance contained nitrogen. If nitrogen quantity is scarce, the solution turns green and a blue precipitate falls out only in time.

Test for Halogens.

Acidify the other half of the alkaline liquid with concentrated nitric acid. If the original substance contains sulphur or nitrogen, the obtained acid solution should be boiled for a few minutes (*in a hood*) to oxidize and remove hydrogen sulphide and hydrocyanic acid that will otherwise interfere with the further reaction. Add a few drops of silver nitrate to a part of the cooled clear acid liquid.

Precipitation of heavy flakes (silver halide) indicates the presence of a halogen.

Silver chloride is white (darkens in the light), silver bromide is yellowish, and silver iodide is yellow.

If it is necessary to identify iodine or bromine, add 1 ml of chloroform or benzene to the remaining portion of the acid solution and then, with shaking, add 2-3 drops of 1 per cent solution of potassium permanganate. Allow the mixture to stand, and observe the colour of the organic layer: the violet colour indicates the presence of iodine,

and yellow or orange, of bromine. Excess of the permanganate can however produce violet colour in the aqueous layer, which should not be mistaken for the positive reaction to the presence of iodine.

To detect nitrogen, sulphur, or the halogens, it is necessary normally to decompose completely an organic substance by ignition with alkali, e.g. with soda lime. Sulphur and the halogens are converted by this reaction into mineral salts—sulphides and chlorides (bromides, iodides), and the greater part of nitrogen is isolated as ammonia. All these substances can be detected by usual ionic reactions. The halogens can often be split off and converted into halides by the action of metallic sodium on an alcoholic solution of the test substance (Stepanov's method, see Experiment 33).

In 1843 Lassaigne suggested the method by which nitrogen, sulphur, chlorine, bromine, and iodine can be detected in an organic substance by igniting it with a pellet of sodium. Sulphur and halogens are bound as in igniting with alkali. Nitrogen partially forms hydrocyanic acid with carbon and sodium, which shows by the formation of complex cyanide, Prussian blue:

$$FeSO_4 + 2NaCN \rightarrow Fe(CN)_2 + Na_2SO_4$$
$$Fe(CN)_2 + 4NaCN \rightarrow Na_4[Fe(CN)_6]$$
$$3Na_4[Fe(CN)_6] + 2Fe_2(SO_4)_3 \rightarrow Fe_4[Fe(CN)_6]_3 + 6Na_2SO_4$$

Traces of ferric salts are practically always contained in green vitriol because it is partially oxidized with atmospheric oxygen. As the alkaline solution containing ferrous hydroxide is boiled, the latter is also readily oxidized. It is not therefore necessary to add ferric salts to the mixture.

It is very difficult to detect nitrogen in nitro compounds by this method.

The detection of sulphur is based on the conversion of the obtained sodium sulphide into dark brown lead sulphide insoluble in alkalis.

$$Pb(NO_3)_2 + 4NaOH \rightarrow 2NaNO_3 + 2H_2O + Pb(ONa)_2$$
$$Na_2S + Pb(ONa)_2 + 2H_2O \rightarrow PbS + 4NaOH$$

Sodium nitroferricyanide, $Na_2[Fe(CN)_5NO]$, reacts with sodium sulphide to form an unstable violet complex, the structure of which is presumably $Na_3[Fe(CN)_5ONSNa]$.

Insufficient boiling with nitric acid, after calcining with sodium, can fail to remove H_2S and HCN (in the test for halogens). Then the addition of silver nitrate can produce a black precipitate of Ag_2S or a white precipitate of AgCN; the appearance and the colour of the latter are very much like those of silver chloride, but it does not darken on exposure to light for a few minutes.

In an acid medium, permanganate oxidizes halide ions to free halogens:

$$2MnO_4^- + 10I^- (Cl^-,\ Br^-) + 16H^+ = 2Mn^{2+} + 5I_2(Cl_2,\ Br_2) + 8H_2O$$

Bromine and iodine readily dissolve in organic solvents to give them specific colours (see Experiment 53).

Some organic substances, e.g. CH_3NO_2, $CHCl_3$, CCl_4, salts of diazonium, di- and trinitro compounds, can explode when ignited with sodium metal, and should not therefore be used in Experiment 16.

17
Beilstein's Test for Halogens

REAGENTS

Not very volatile organic substances containing halogen, e.g. *chlorobenzene*, *bromobenzene*, *chloroacetic acid*, *iodoform*, etc.

Make a 1-2 mm loop at the end of a thin red copper wire and ignite it in the colourless flame of a burner until the flame is no longer tinged green. Cool the blackened wire loop, take a drop or a few grains of the test substance with it, and introduce the loop again into the hottest part of the colourless flame. The presence of halogens is shown by the green colour of the flame.

To clean the wire, wet it with hydrochloric acid and ignite again. If the flame is insufficiently hot (for example, the flame of a spirit burner), fix a grain of copper oxide in the loop or a copper spiral.

This method for detection of halogen in an organic compound was suggested in 1872 by the Russian scientist Academician F. K. Beilstein. The colouration of the flame is explained by the formation of copper halides, which become volatile at high temperatures.

This test is very sensitive and can detect even traces of halogen in a substance. It can be used, for instance, for detecting chlorine in saliva.

Some nitrogenous substances that are free from halogen, tinge the flame as well, but this is perhaps through the formation of copper cyanide. Examples of such substances are derivatives of pyridine, quinoline, carbamide, and others (see also Experiment 55).

The Beilstein's test fails to detect fluorine, since copper fluoride is non-volatile.

CHAPTER FOUR

SATURATED AND UNSATURATED HYDROCARBONS

Methane, ethylene, acetylene will be used as saturated and unsaturated gaseous hydrocarbons (see Experiments 23-26). Liquid hydrocarbons, specially prepared for the experiment, are more convenient.

A. *Mixture of liquid saturated hydrocarbons (alkanes).* Shake commercial kerosene or gasoline in a separatory funnel with concentrated sulphuric acid (one volume of the acid per 10 volumes of the hydrocarbons) for 5-10 minutes. Shake first carefully (liberation of heat is possible) and then vigorously. Turn periodically (first more often) the funnel upside down and open slightly the tap to release gas and vapours. Allow the mixture to stand and remove the acid layer through the tap. Repeat the operation two or three times adding new portions of the acid, then an alkaline solution of potassium permanganate, and finally water. Dry the purified mixture of saturated hydrocarbons, for instance, by granular calcium chloride, and use it for the experiments. The mixture should not react to the double bond test (see Experiments 18 and 19), but the presence of cyclic hydrocarbons, naphthenes, does not practically affect the course of the reactions described below.

Kerosene (gasoline), which is usually coloured yellow by impurities, often becomes colourless after such a treatment. If the liquid is not fully colourless, distil kerosene (gasoline) and collect the colourless fraction within a wide range of temperatures. Purify the distillate with sulphuric acid.

Commercial "petroleum ether" practically does not contain unsaturated compounds and it can therefore be often used as the mixture of saturated hydrocarbons. Colourless mineral oils (paraffin or Vaseline oil), diluted with one of the listed substances can also be used (after checking for the absence of unsaturated compounds).

B. *A mixture of liquid unsaturated hydrocarbons, predominantly alkenes.* Commercial gasoline and kerosene contain some quantities

of unsaturated hydrocarbons (cracked gasoline contains considerable quantities) and therefore give all typical qualitative reactions of unsaturated hydrocarbons. If these petroleum products are colourless, they can be used in the experiment without purification. Coloured gasoline or kerosene should first be distilled and the colourless fraction collected within a wide temperature range.

If isoamyl alcohol is available, a mixture of liquid pentenes can be prepared for studying reactions of unsaturated hydrocarbons. To prepare the mixture, boil 15 volumes of technical amyl (predominantly isoamyl) alcohol and 1 volume of concentrated sulphuric acid for a few hours in a flask with a reflux condenser. The temperature of water in the reflux condenser jacket should be 60-80 °C. In these conditions, the vapours of isoamyl alcohol and of diamyl ether are condensed and returned into the flask, while the vapour of pentene (to be more exact, the vapours of pentenes) and partly of water pass into another long descending condenser. Cool the receptacle of liquid pentene with ice or snow. Separate the upper layer of the condensate, wash with alkali, and dry with calcined sodium sulphate.

A better dehydrating agent for isoamyl alcohol is phosphoric acid. Heat 100-150 g of syrupy phosphoric acid in a porcelain dish to a temperature of 220 °C (a thermometer in the liquid), cool slightly, and transfer into a flask equipped with a reflux and a straight-run condenser (see above). Heat the acid to 230-250 °C on a sand bath, and slowly add isoamyl alcohol from a funnel. Collect the condensate as described above. The obtained product, technical pentene, can be used without further purification in the test for double bonds. It contains mainly 3-methyl-2-butene (trimethylethylene), $(CH_3)_2C=$ $=CHCH_3$ (b.p. 38 °C). For Experiment 21, distil pentene to collect the fraction boiling out at temperatures below 50 °C. The yield of the distilled pentene is 30-40 per cent of the initial mass of the alcohol.

Turpentine can also be used in Experiments 18, 19, 20, and 22 as an unsaturated hydrocarbon. Its main components, $C_{10}H_{16}$ hydrocarbons, are unsaturated. Of these components, pinene has one double bond and other isomers, two double bonds.

In Experiments 18 and 19, 10-20 per cent solutions of pentene or turpentine in gasoline can be used as well.

When giving off the required materials to the students (the same material can have different codes) it is reasonable to give also individual tasks, e.g. to make out the equations of the reactions for a particular hydrocarbon that can supposedly be present in the given material: alkane (certain) isomers of pentane, hexane, heptane, octane), and the corresponding alkene.

While studying the properties of various hydrocarbons, it is necessary to note their sparing solubility in water and to compare

their attitude towards halogens, oxidants, concentrated sulphuric and nitric acids. Each experiment described in this chapter should be carried out with both saturated and unsaturated hydrocarbons; the course of the reaction should be described in the notebook to illustrate the difference in chemical properties of the compounds belonging to these classes.

The difference in properties of saturated and unsaturated hydrocarbons can be observed using the simplest individual gaseous hydrocarbons (methane, ethylene, and acetylene). The specific reagents in this case are bromine water and alkaline solution of potassium permanganate. The reaction with concentrated acids is less illustrative. The difference in the composition of these hydrocarbons also shows in the character of their burning.

Acetylene is suitable for illustrating the formation of metal derivatives of hydrocarbons containing the —C≡CH group.

18
Bromination of Hydrocarbons

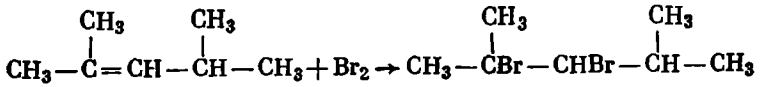
REAGENTS

Saturated hydrocarbons, liquid.
Unsaturated hydrocarbons, liquid.

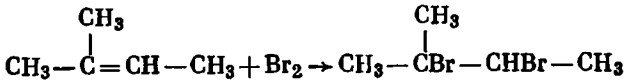
Place 1 ml of a hydrocarbon or a mixture of hydrocarbons into a dry test tube and add, drop by drop, bromine solution with slightly shaking the test tube. If the yellow colour does not vanish in the cold, heat the mixture slightly. Establish whether disappearance of the colour, caused by the presence of free bromine, is accompanied by the formation of hydrogen bromide (gas), having a pungent odour, fuming in the air (especially if a rod dipped in ammonia is introduced into the test tube), and colouring red a wet blue litmus test paper. Evolution of hydrogen bromide is especially vivid against a black background if the test tube is shaken and if air is blown over its mouth.

Addition of bromine at multiple (double, triple) bonds, which is characteristic of unsaturated hydrocarbons, is very fast and the solution is decolourized. In many cases bromine can replace hydrogen atoms (particularly at tertiary carbon atoms) in various hydrocarbons. This process of substitution also decolourizes the solution, but is much slower than in the case of addition, and requires heating, illumination, or a catalyst; moreover, the process is accompanied by evolution of hydrogen bromide. This is very important since the liberation of hydrogen bromide often becomes vivid only on illumination of the reaction mixture with sunlight or intense electric light.

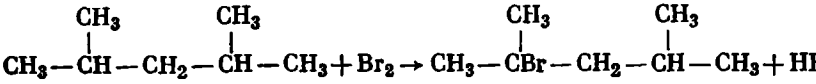
The reactions of bromination of alkanes and alkenes are as follows:



2,4-dimethyl-2-pentene — 2,3-dibromo-2,4-dimethylpentane



2-methyl-2-butene (trimethylethylene) — 2,3-dibromo-2-methylbutane



2,4-dimethylpentane — 2-bromo-2,4-dimethylpentane

Products of further bromination and other isomeric bromine-substituted alkanes can be produced simultaneously as well.

The mechanisms of these reactions can be different. The electron concepts of the mechanisms of reactions in organic chemistry were first developed in 1913 by the Russian scientist A. M. Berkenheim (1867-1938), but later the theory was fully worked out by the English chemists Lewis, Ingold, and others. The abbreviations used in designation of the reactions are as follows: *S*—substitution, *E*—elimination, *A*(*Ad*)—addition, *N*—nucleophile (donor of electron pair), *E*—electrophile (acceptor of electron pair), and *R*—radical (neutral particle containing an unpaired electron).

Bromination of alkanes is the reaction of the radical substitution type and is a chain process. Free bromine atom, produced by dissociation of a bromine molecule under the action of heat or light energy, contains an unpaired electron, i.e. is a free radical. It splits off the hydrogen atom from the alkane molecule, which itself turns into a free radical. The latter splits a new bromine molecule and joins with one of its atoms to form hydrogen halide. Another bromine atom reacts with the next alkane molecule, and the process is thus continued.

The mechanism of the reaction changes in the presence of a catalyst, and the process can be electrophilic substitution (see explanations to Experiment 151).

The first step of bromine addition across the double bond of the alkene molecule is perhaps the shift of the electron pair of the π-bond with simultaneous polarization of the bromine molecule and formation of the molecular alkene-halogen complex. Its further conversion into dibromide can proceed (depending on the properties of the medium and other conditions) by the ionic, radical, or molecular mechanism. Bromination of alkene in a non-polar organic solvent

is usually regarded as the A_E reaction (electrophile, the positive ion of bromine that is added the first), or A_R reaction (particularly with illumination) with addition first of one bromine atom and formation of a free organic radical (see above) and continuation of the chain reaction. These processes having different mechanisms can proceed simultaneously.

Bromine solutions in organic solvents are especially suitable for bromination reactions since they produce with hydrocarbons a homogeneous mixture. The reaction is faster, and isolation of hydrogen bromide, which is insoluble in this medium, is quite apparent, which indicates that the substitution reaction has taken place. In the majority of cases bromine water is less convenient for work with liquid substances, because the bromination reaction is slow, requires frequent energetic shaking, and the formation of hydrogen bromide, well soluble in water, is impossible to detect. Finally, bromine water often acts not only as a brominating agent, but also as an oxidant, which makes it difficult to interpret the cause of decolouration of the reaction mixture. Bromine water is more convenient for work with gases. Bromination of hydrocarbons is accelerated under the action of light and in the presence of some catalysts (cf. Experiments 149 and 150).

If, under specified conditions, only the first drops of bromine solution are decolourized quickly, this does not indicate that the test substance contains double bonds. Actually, the calculations by the molecular mass indicate, for instance, that to brominate 1 g of heptene (mol. wt. 98) across the double bond, about 1.6 g of bromine is needed (at. wt. 80), i.e. about 50 g of its 3 per cent solution. Hence the rapid decolouration of the first 2-5 drops of bromine solution in 1 ml of a mixture of hydrocarbons can be the result of the presence of negligibly small quantities of unsaturated compounds (of the order of decimal fractions of a per cent).

If the quantity of bromine (that is added until its binding is discontinued), can be accurately determined, the bromination reaction can be used with hydrocarbons and other organic substances not only for quantitative determinations of unsaturated compounds, but also for determining the degree of unsaturation (the number of multiple bonds) of pure individual compounds. But amines, phenols, most secondary and tertiary alcohols, aldehydes, and ketones, also rapidly decolourize bromine solutions, even if they do not contain multiple bonds. Amines often react without isolation of HBr. Bromination across the double bond usually becomes very difficult if electronegative groups are accumulated at the carbon atoms of this bond. For example, phenylethylene (styrene), $C_6H_5CH=CH_2$ is brominated rapidly; diphenylethylene (stilbene), $C_6H_5CH=CHC_6H_5$, slowly; and triphenylethylene, $(C_6H_5)_2C=CHC_6H_5$, trichloroethylene, and tetrachloroethylene (C_2HCl_3 and C_2Cl_4) are not brominated at all.

Brominated very slowly are also many unsaturated acids, e.g. maleic, fumaric, and cinnamic. It is often explained by the specific inhibiting action of atmospheric oxygen on the course of the radical reaction. For example, bromination of cinnamic acid in a medium of an inert gas is very fast.

19
Oxidation of Hydrocarbons with Potassium Permanganate (Wagner's Reaction)

REAGENTS

Saturated hydrocarbons, liquid.
Unsaturated hydrocarbons, liquid.

To 1 ml of a test substance, add an equal volume of soda solution and then, gradually, drop by drop and with strongly shaking, potassium permanganate solution until the appearance of the mixture no longer changes.

Oxidation of unsaturated compounds with potassium permanganate was first studied by A. M. Zaitsev in 1873, but later, in 1886-1888, in more detail, by another outstanding Russian scientist E. E. Wagner, and almost at the same time by A. Bayer in Germany.

If only saturated hydrocarbons are present, the violet colour of the aqueous layer produced by the first drops of potassium permanganate does not change.

Unsaturated hydrocarbons are detected by the disappearance of the initial colour of permanganate and by the precipitation of brown flakes. If the oxidation is slow or the concentration of unsaturated compounds is insignificant, the violet colour turns brownish red.

In an alkaline solution, permanganate can give off oxygen, up to three equivalent weights per molecule of $KMnO_4$; manganese dioxide is isolated in this case.

As in the case with bromination (see Experiment 18), even very small quantities of unsaturated compounds in a mixture change the colour of the first drops of the reagent. Solid and liquid substances can be studied by this method in solutions or suspensions in water, acetone, etc.

As manganese dioxide accumulates in the mixture, it sometimes masks the colour changes. To remove the masking effect of the precipitate, dip a strip of filter paper into the mixture. The paper will absorb only the solution, and its colour will be apparent.

Oxidation of unsaturated compounds with permanganate is accompanied by the formation of glycol and alkali:

$$3>C=C<+2KMnO_4+4H_2O \rightarrow 3>\underset{OH}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}<+2MnO_2+2KOH$$

For example, the reaction for the heptene mentioned above is as follows:

$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-\overset{CH_3}{\overset{|}{CH}}-CH_3+O+H_2O \rightarrow CH_3-\overset{CH_3}{\overset{|}{C}}(OH)-CH(OH)-\overset{CH_3}{\overset{|}{CH}}-CH_3$$

2,4-dimethylpentane-2,3-diol

2-Methyl-2-butene is oxidized with permanganate in these conditions to 2-methylbutane-2,3-diol.

Oxidation process is often continued further to give aldehydes, ketones, and mainly acids. The molecule of the original compound is split across the multiple bond. Manganese dioxide catalyses the oxidation of organic compounds in the conditions described above, and for this reason the oxidation of substances (containing double- or triple-bonded carbon atoms) with alkaline solution of potassium permanganate is first slow, but as MnO_2 is accumulated, the oxidation is usually accelerated. Some compounds that do not contain multiple bonds, e.g. formic, oxalic, and citric acids, aldehydes, phenols, many ketones, glycerol, are also rapidly oxidized with this reagent. But most saturated compounds, saturated hydrocarbons included, do not react with an alkaline solution of $KMnO_4$, or react very slowly. There are also rare exceptions among unsaturated compounds that are stable towards the action of potassium permanganate.

20
Reaction of Hydrocarbons with Concentrated Sulphuric Acid

REAGENTS

Saturated hydrocarbons, liquid.
Unsaturated hydrocarbons, liquid.

Add 1 ml of concentrated sulphuric acid to 1 ml of a mixture of hydrocarbons and shake strongly (but carefully) for a few minutes, cooling the test tube in water. Note the different attitude of saturated and unsaturated hydrocarbons towards concentrated sulphuric acid.

21
Polymerization of Pentene

REAGENTS

Pentene (see the beginning of Chapter 4).
Sulphuric acid, 75 per cent solution.

To prepare 75 per cent solution of sulphuric acid, add 6 ml of concentrated sulphuric acid, density 1.84 g/cc, to 3 ml of water, and cool the hot mixture.

Place 8 ml of pentene in a 30-50 ml long-neck flask, provided with a ground-in stopper (e.g. a 50-ml volumetric flask), and cool in a mixture of snow and salt to −5 or −10 °C. Add 6 ml of 75 per cent sulphuric acid cooled to the same temperature. Shake the mixture strongly and frequently for 30 minutes with cooling. Open the stopper from time to time. Then shake for another 30-60 minutes without cooling. The mixture is first readily separated into two layers. The upper layer gradually diminishes and finally almost completely disappears.

Heat the thickened mixture on a boiling water bath for 10-15 minutes. The mixture is delaminated again but, unlike the starting pentene, the upper layer is not volatilized on heating.

Cool the mixture and remove the lower acid layer using a pipette. Wash the remaining hydrocarbon layer in the same flask (or in a wide test tube) first with an equal volume of soda solution, then with an equal volume of water (each time removing the lower layer with a pipette), and dry with a few pieces of calcium chloride. Transfer the clear liquid to a test tube with a side arm and a thermometer for 250 °C and distil without a condenser. A few drops are distilled at temperatures below 150 °C. The main fraction boils out at 153-163 °C. It is an odourless mixture of pentene dimers, i.e. isomeric decenes, $C_{10}H_{20}$. Fractions boiling at higher temperatures contain trimers, pentadecenes, $C_{15}H_{30}$. All fractions clearly react in the test for the double bond (see Experiments 18 and 19).

In conditions of Experiment 20, saturated hydrocarbons do not react with sulphuric acid, while unsaturated compounds react very rapidly with evolution of heat. The acid layer turns brown and the hydrocarbon layer diminishes in volume and can dissappear.

In the cold, and with good stirring, sulphuric acid is added to the double bonds of hydrocarbons to form alkyl sulphuric acids having the general formula $ROSO_2OH$ (see Chapter 6) which are well miscible with sulphuric acid. The starting volume of the hydrocarbon mixture decreases as a result. The hydrogen atom of sulphuric acid attaches itself to the double-bonded carbon atom united to the

greater number of hydrogen atoms, while the acid radical (OSO_2OH) is added to the neighbouring atom. This general rule explaining the addition of acids (both oxy- and hydrohalic acids) to the double bonds was formulated by Markownikoff in 1868-1876, and developed later by Zaitsev. Molecules of asymmetric alkenes have a dipole moment, i.e. their double bond is polarized with alkyl groups that produce a positive inductive effect. The result of this effect is that the electron density is higher at the carbon atom united to the greater number of hydrogen atoms (out of the double-bonded carbon atoms). The attack of the cation of the reagent (the hydrogen ion in this particular case) is directed to this carbon atom. Markownikoff's rule does not hold for hydrogen bromide addition reactions if peroxides are present.

With increasing temperature, alkyl sulphuric acid can be attached to the double bond of the new olefin molecule; and subsequent elimination of H_2SO_4 produces a dimer of the starting hydrocarbon that again contains the double bond. Repetition of this process produces more complicate sparingly soluble polymerization products (sometimes coloured and resin-like). Unsaturated hydrocarbons can thus be removed from their mixture with saturated compounds by the action of strong sulphuric acid (see page 76).

The polymerization reaction can be maintained at the stage where the dimer is predominantly produced, by lowering the concentration of sulphuric acid and decreasing the reaction temperature.

2,3,4,4-Tetramethyl-2-hexene predominates in a mixture of decenes (Experiment 21). The quantity of trimers, and especially high polymers, which are produced in these conditions, is markedly smaller.

If sulphuric acid used in the experiment is less concentrated, the alkyl sulphuric acid, that is first formed, does not react with the second molecule of ethylene hydrocarbon, but undergoes hydrolysis to form alcohol.

Polymerization of ethylene hydrocarbons under the action of sulphuric acid was discovered in 1877 by A. M. Butlerov, and further studied by A. E. Favorskii. In 1932-1937, S. S. Nametkin established that alongside with the Butlerov polymerization, another polymerization takes place, "hydrodehydropolymerization". By this reaction olefin converts into a mixture of polymeric saturated and unsaturated hydrocarbons.

Not only olefins but also alcohols, phenols, ethers, and other compounds are dissolved in cold concentrated sulphuric acid, or appreciably react with it. In 1873 Butlerov showed that saturated and aromatic hydrocarbons, and their halogen derivatives, are stable to this reagent at low temperatures. The simplest olefin, ethylene, well dissolves in sulphuric acid at 80 °C to give ethylsulphuric acid, but is very slowly polymerized by the acid. Many methods have

been developed in the past years by which ethylene can be polymerized using various catalysts. Solid and elastic polyethylene (polythene) is widely used for domestic purposes and in industry in the form of various products (films, tubes, containers, etc.).

When strongly heated, concentrated sulphuric acid slowly oxidizes and sulphonates hydrocarbons of all types, including saturated hydrocarbons.

22
Reaction of Hydrocarbons with Concentrated Nitric Acid

REAGENTS

Saturated hydrocarbons, liquid.
Unsaturated hydrocarbons, liquid.

To 1 ml of a test substance, add 1 ml of concentrated nitric acid and shake the mixture, first with care, and then energetically for a few minutes. Note the different attitude of saturated and unsaturated hydrocarbons to the acid.

As nitric acid acts on unsaturated hydrocarbons, the mixture turns brown and heat is liberated (sometimes much heat). Saturated hydrocarbons do not change in these conditions.

A complicate mixture of products (some of them resinous) is formed in the reaction of unsaturated hydrocarbons with nitric acid. The acid reacts with saturated hydrocarbons only at high temperatures. In 1888-1893, M. I. Konovalov established that dilute nitric acid reacts with hydrocarbons in these conditions to give nitro compounds of hydrocarbons having the general formula $R—NO_2$ (Konovalov's reaction). The reaction was later studied in detail by Nametkin, who showed that in many cases isonitro compounds having the formula $RCH=N\begin{matrix}\nearrow O\\ \searrow OH\end{matrix}$ (see Experiment 108) are first produced. P. P. Shorygin, A. V. Topchiev, A. I. Titov (USSR), and C. Ingold (Great Britain) discovered later the details of the intricate process of nitration.

Nitro groups are more readily substituted for hydrogen atoms at the tertiary or secondary carbon. Konovalov's reaction occurs by the radical mechanism and begins with the attack of nitrogen dioxide NO_2 on hydrocarbon; the NO_2 radical (containing an unpaired electron) is easily liberated by heating nitric acid.

At the present time, nitration of saturated hydrocarbons at high temperatures is widely used in industry, and nitro compounds of the fatty series are valuable intermediates for the manufacture of

substances of other types. For example, nitro compounds can be used to produce carboxylic acids and hydroxylamine:

$$R-CH_2NO_2 \xrightarrow{+H_2O} R-COOH+NH_2OH$$

23
Formation of Methane and Its Properties

REAGENTS

Potassium acetate, *sodium acetate* or *calcium acetate* (anhydrous).
Soda lime.
Bromine water, dilute solution, yellow.
Potassium permanganate, strongly diluted solution.

Of the above listed acetates, potassium acetate suits the purpose best of all: methane is produced very rapidly, and the process is smooth, almost without any side reactions. Potassium acetate crystals are anhydrous and normally do not require drying.

To dry sodium acetate, carefully fuse the crystal hydrate, $CH_3COONa \cdot 3H_2O$, in an iron vessel until the material, which first becomes solid after removal of water, begins to melt again. (Heat carefully to avoid charring.) Allow the hygroscopic product to cool, grind slightly, and keep in a well stoppered container.

Calcium acetate often contains 1 or 2 molecules of water of crystallization, and it should therefore be dehydrated by heating to 120-130 °C.

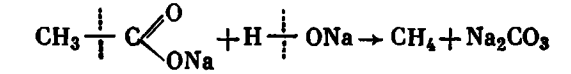
Commercial soda lime should be preliminarily strongly heated and then cooled in a desiccator. It can be prepared by mixing powdered unslaked lime with 1/2 weight of a saturated solution of sodium hydroxide, evaporating and calcining the mixture.

Small quantities of methane and ethylene can easily be produced in a test tube with a short outlet tube inserted in a stopper (or on a rubber ringlet). Connect a 10-12 cm long rubber tubing, with a glass end-piece, to the gas outlet tube. This flexible structure will facilitate the work.

Mix anhydrous acetate with two parts by weight of soda lime, grind the mixture thoroughly in a mortar, and place a few grams of the mixture in a dry test tube. Fix the test tube in a horizontal position, connect the gas outlet tube, and heat the mixture over the flame of a burner, first carefully, and then strongly. Lower the outlet tube alternately into test tubes containing bromine water and potassium permanganate. Note if the colour of these reagents changes as the produced gas is bubbled through them. In other words, establish whether methane is brominated or oxidized.

Without interrupting the heating, collect methane in a test tube filled with water and turned upside down in a beaker or a bath containing water. Remove the gas outlet tube from water and discontinue heating. Close the test tube with a finger tip, put it close to the flame of a burner, and release the finger. Methane burns quietly, producing a bluish flame. If so, the flame can be put to the orifice of the gas outlet tube. Put a porcelain plate (dish, crucible lid) into the flame of the burning methane: black soot is not deposited on the cold surface (cf. Experiment 24).

The formation of methane from an acetate and soda lime (a mixture of hydroxides of sodium and calcium) is an example of the general reaction for preparing hydrocarbons from salts of carboxylic acids by heating them with alkali. The reaction is as follows:



Soda lime is more convenient because, unlike sodium hydroxide, it does not affect glass, does not melt on heating, and, owing to its porosity, facilitates liberation of methane. Side products of this reaction are acetone (see Experiment 67), hydrogen, ethylene, and carbon dioxide.

In the conditions of the experiment, methane reacts neither with bromine, nor with potassium permanganate. If methane is passed for a long time into bromine water, the latter can be discoloured because volatile bromine will be captured by the gas current, and because bromine is decolourized by ethylene. In the experiments illustrating the reaction of gaseous substances with liquid reagents, the gas outlet tube should from time to time be removed from the test tube, the latter closed tightly and shaken strongly.

24
Formation of Ethylene and Its Properties

REAGENTS

Ethyl alcohol, crude or rectified.

Bromine water, dilute, pale yellow.

Potassium permanganate, strongly diluted, bright pink aqueous solution.

Prepare ethylene in the same apparatus as was used for preparing methane (Experiment 23), except that a short (5-6 cm) glass tube, containing fine grains of soda lime placed between two cotton wool pads, is incorporated between the glass tube in the stopper and a rubber tube with an end-piece.

Place 1 ml of alcohol in a test tube, and add carefully, with shaking, 4 ml of concentrated sulphuric acid. Add a boiling stone into the hot mixture (Experiment 4) to prevent ebullition, connect the gas outlet tube, and heat slowly and carefully the test tube until gas begins smoothly evolving. The reaction mixture darkens. Proceed as instructed in Experiment 23. Use the liberating gas for the same tests as in the case with methane.

Unsaturatedness of ethylene shows itself in the rapidity of its bromination and oxidation, and also in a brighter flame as compared with the colour of the methane flame. A black spot of soot appears on a porcelain plate put into the flame of ethylene.

Ethylene is produced as a result of thermic destruction (at 170 °C) of ethylsulphuric acid, which is formed in the reaction of alcohol and sulphuric acid (cf. Chapter 6):

$$C_2H_5OH + HOSO_2OH \rightleftharpoons C_2H_5O-SO_2OH + H_2O$$

$$H-\overset{|}{\underset{|}{C}}H_2-CH_2-\overset{|}{\underset{|}{C}}H-OSO_2OH \rightleftharpoons H_2SO_4 + H_2C=CH_2$$

probably with intermediate formation of carbonium ion (see explanations of Experiment 27).

To accelerate dehydration of alcohol in the production of large quantities of ethylene using sulphuric acid, a catalyst, e.g. anhydrous aluminium sulphate, copper sulphate, alums or sand, tripoli, pumice, or fired clay, should be added. Phosphoric acid can be used in the process instead of sulphuric acid. In this case, the process of ethylene formation (like of the other olefins) is the same as with sulphuric acid, but the process is more quiet, and no catalysts are required even for the manufacture of large quantities.

Concentrated sulphuric acid is an oxidant. As the reaction mixture is heated, in addition to ethylene and traces of ether $(C_2H_5)_2O$, formed also are products of oxidation of organic substances, e.g. CO, CO_2, and carbon (the liquid in the test tube blackens). Sulphuric acid is reduced to sulphurous acid anhydride, which decolourizes solutions of bromine and potassium permanganate (like ethylene). Ethylene is therefore passed through soda lime to bind SO_2 and CO_2. Alkali solution can be used instead of soda lime, but the apparatus will be more complicated. It is unnecessary to remove carbon monoxide from ethylene, since it does not react with bromine water or potassium permanganate. The reactions of ethylene with these reagents were discussed in Experiments 18 and 19. The bright colour of ethylene flame, and deposition of carbon black resulting from incomplete combustion of ethylene result from the high percentage content of carbon.

25
Formation of Acetylene and Its Properties

REAGENTS

Calcium carbide, lumps.
Bromine water, pale yellow dilute solution.
Potassium permanganate, strongly diluted, bright pink solution.

Carry out experiments with acetylene in the HOOD, since acetylene impurities have unpleasant odour (mainly hydrogen phosphide) and are harmful.

Small quantities of acetylene can be prepared in a test tube having a hole in the bottom. Fix the test tube in the stand in the vertical position. Place glass wool on the test tube bottom, then put 3-4 lumps of calcium carbide, and close with another glass wool pad. Close the test tube with a stopper through which a gas outlet tube provided with a screw clip is passed. Close the screw clip, and immerse the test tube into water in a beaker or a bottle so that the water level is much above the carbide bed. As the clip is now opened, water enters the test tube through the hole in the bottom, and the formed acetylene passes into the gas outlet tube. As the clip is closed, the reaction stops. Production of acetylene can thus be easily controlled.

Carry out experiments with acetylene as described in Experiments 23 and 24: observe bromination, oxidation, and burning of acetylene. The unsaturatedness of acetylene shows in these experiments more vividly than with ethylene.

The reaction of formation of acetylene is exothermic

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + HC \equiv CH + 139 \text{ Kcal}$$

In the formation of large quantities of acetylene, the reaction can be too vigorous. To ensure quiet and uniform production of acetylene, use a mixture of equal volumes of water and alcohol instead of pure water. Or use a saturated solution of table salt.

Solubility of acetylene in water is much higher than that of ethylene or methane. At room temperature and atmospheric pressure, the solubility of acetylene (per volume of solvent) is 1 volume in water, 4 volumes in benzene, 6 volumes in alcohol, and 25 volumes in acetone.

Upon addition of bromine to acetylene, dibromoethylene, $CHBr{=}CHBr$, is first formed, and then tetrabromoethane, $CHBr_2{-}{-}CHBr_2$. As acetylene is oxidized with potassium permanganate in an acid and neutral medium, CO_2 and formic acid are mainly produced, and in an alkaline medium, first glycolic aldehyde, CH_2OHCHO, and then oxalic acid, HOOC—COOH, are formed.

26
Formation of Metal Derivatives of Acetylene

REAGENTS

Acetylene (see the previous Experiment).
Silver oxide, ammonia solution.
Cuprous oxide.
Ethyl alcohol, crude or rectified.

Prepare silver oxide solution in ammonia by adding aqueous ammonia by drops to silver nitrate solution until the precipitate, that first falls out, is dissolved.

Prepare cuprous oxide solution in ammonia by adding 1-2 ml of concentrated aqueous solution of ammonia and 10 ml of water to 1 g of cuprous chloride and shaking the mixture vigorously. Allow the mixture to stand, decant the solution and keep above metallic copper (shavings or wire).

The blue colour of the ammonia solution of cuprous salt, which indicates the presence of a complex (ammoniate) with Cu^{2+} ion, masks the course of reaction with acetylene. To remove the blue colour, heat the reagent slightly, and add 2-3 drops of a 2 per cent solution of hydroxylamine hydrochloride (or sulphate) until the solution is decolourized.

Much hydroxylamine salt is required if the solution is not heated.

Place 1-2 ml of ammonia solutions of silver and copper salts in two separate test tubes and pass acetylene gas into the solutions. White silver acetylenide and red copper acetylenide precipitate.

Separate copper acetylenide by filtering with suction on a funnel (Fig. 6). Wash the precipitate with a few drops of alcohol, transfer the moist filter with the precipitate onto another, larger piece of filter paper, and dry carefully in a dish on a water or sand bath. Take the dry filter with the copper acetylenide with forceps and put into the flame of a burner: a loud but safe explosion occurs.

Silver acetylenide is *dangerous* to handle. Hence *do not filter it*.

Destroy the remains of acetylenides at the end of the experiment. To do so, place them (together with the filter paper) into a beaker containing water, and add concentrated hydrochloric or nitric acid (1/4-1/5 volume of water).

Metal can be substituted for the hydrogen atom that is attached to the triple-bonded carbon atom (the specific reaction for the group $-C{\equiv}CH$).

The electron clouds of π-bonds strongly overlap. As a result, the hydrogen at the triply bonded carbon is held weaker and is 'protonized' both in acetylene and its homologues containing the group

—C≡CH, and e.g. in hydrocyanic acid H—C≡N. Formation of metal derivative of acetylene is the reaction of electrophilic substitution. Acetylene containing two such hydrogen atoms in a molecule reacts with complex ions of silver ammoniate:

$$C_2H_2 + 2[Ag(NH_3)_2]^+ = C_2Ag_2 + 2NH_4^+ + 2NH_3$$

The reaction of acetylene with ions of cuprous ammoniate, $[Cu(NH_3)_2]^+$, is similar in its character.

Acetylenides of copper and silver are insoluble in water but readily decomposed with acids to liberate acetylene. An explosion of acetylenide produces free carbon and metal in the dispersed state.

Cuprous salts are readily oxidized with atmospheric oxygen. In order to convert divalent copper back into the monovalent state, a strong reducing agent, hydroxylamine, is used:

$$4Cu^{2+} + 2NH_2OH \longrightarrow 4Cu^+ + 4H^+ + N_2O + H_2O$$

An ammonia solution of cuprous salt can be prepared from a cupric salt, but much hydroxylamine is required to reduce divalent copper.

CHAPTER FIVE

HALOGEN DERIVATIVES OF METHANE SERIES HYDROCARBONS

Various halogen derivatives of hydrocarbons can be used in experiments described in this chapter. Major constants of some of them are given in Table 2.

Table 2

Properties of Halogen Derivatives of Methane Series Hydrocarbons

Hydrocarbon	Formula	M. p., °C	B. p., °C	Density, g/cc
Ethyl bromide	C_2H_5Br	−119	38	1.46
Methyl iodide	CH_3I	−64	43	2.28
Ethyl iodide	C_2H_5I	−109	72	1.93
Dichloroethane	$CH_2Cl—CH_2Cl$	−35	84	1.25
Dibromoethane	$CH_2Br—CH_2Br$	10	132	2.18
Chloroform	$CHCl_3$	−63	61	1.49
Bromoform	$CHBr_3$	8	150	2.89
Iodoform	CHI_3	119	sublimes	4.01
Carbon tetrachloride	CCl_4	−23	77	1.59

All these substances are almost insoluble in water. Ethyl bromide, methyl iodide, ethyl iodide, dibromoethane, bromoform, iodoform are prepared in small quantities in the course of the experiments. The others should be ready for use before the experiment.

If a large quantity of a halogen derivative is required for the experiment, prepare ethyl bromide by the widely known method, which is as follows.

Place 110 ml of concentrated sulphuric acid in a round-bottomed flask, add quickly, pouring by the flask neck, 110 ml of ethyl alcohol (crude or rectified) with shaking, and cool the mixture. Add carefully 75 ml of ice-cold water and 100 g of potassium bromide powder.

Continue shaking and cooling the flask in water. Connect a long condenser, and distil the mixture on a sand bath, heating the flask first carefully (to prevent foaming), and then intensely. Collect the distillate in a receptacle containing water and pieces of ice (snow). The end of the distillate outlet tube should be immersed in water to 1-1.5 cm.

Adjust the distillation rate so that heavy drops of ethyl bromide fall incessantly into the water of the receptacle. See to it that the liquid does not rise from the receptacle into the condenser.

When ethyl bromide distillation is over, stop heating. Transfer the receptacle contents into a separating funnel, separate the heavy layer of ethyl bromide, and wash it 1-2 times with water. The yield should be about 80 g. Keep ethyl bromide under water. The obtained product can be used in the experiments without additional purification. Dehydration can be done with calcium chloride.

If ethyl bromide should be purified (mainly from ethyl ether), wash it carefully with concentrated sulphuric acid (Experiment 52) and distil on a water bath. Collect the fraction boiling out at temperature from 35 to 40 °C.

27
Preparing Ethyl Bromide

REAGENTS

Ethyl alcohol, crude or rectified.
Potassium bromide, powder.

Place 3 ml of alcohol into a wide test tube provided with a stopper and a side arm, and add 3 ml of sulphuric acid with shaking. Cool the hot mixture, add 2 ml of water, cool again, and add 3 g of potassium bromide powder while shaking the tube contents. Connect a tube to the side arm and fix the test tube in an inclined position in the stand. Lower the end of the outlet tube into another test tube (receiver) containing 1 ml of water and a piece of ice (snow). Keep this test tube in a beaker containing a mixture of water and snow. Heat the test tube contents carefully to boiling over a burner, first heating the upper layers of the liquid. The mixture should boil quietly and uniformly. Distil for 10-12 minutes and stop heating when potassium bromide crystals disappear, and when heavy drops of ethyl bromide cease falling into the receptacle.

Remove the greater part of the upper aqueous layer from the receptacle. Add cold pure water, close the test tube tightly, shake, and allow to settle. The yield of ethyl bromide is 1-1.5 ml.

Collect the obtained ethyl bromide using a pipette (see Experiment 3) and use in the experiment, or transfer into a dry clean test tube with a side arm, dry with a piece of calcium chloride, and

distil with a thermometer through a straight-run condenser into a cooled receptacle. The yield is about 1.5 g, which is 50-60 per cent of theory, calculating as potassium bromide.

Dip a glass rod into ethyl bromide and put it into the flame of a burner: the flame is tinged green on its margins. The colour is characteristic of alkyl halides.

The preparation of ethyl bromide is an example of the reaction in which halogen is substituted for the hydroxyl of alcohol by the action of hydrogen halide:

$$C_2H_5OH + HBr \rightleftharpoons H_2O + C_2H_5Br$$

In this reaction hydrogen bromide is formed by the action of sulphuric acid on potassium bromide. Excess quantities of the acid bind water that is formed in the reaction, and the other reaction product, ethyl bromide, is distilled and also removed from the reaction zone. The equilibrium is thus shifted to the right, and the process is markedly accelerated. Part of alcohol first produces ethylsulphuric acid (see Chapter 6), which also reacts with hydrogen bromide:

$$HOSO_2OC_2H_5 + HBr \rightarrow H_2SO_4 + C_2H_5Br$$

Ethyl ether, ethylene, carbon dioxide, and sulphurous anhydride are side products in this reaction (see Experiments 41-43).

Formation of ethyl bromide is the nucleophilic substitution of the S_N2 type.* Bromide anion is the nucleophile. The proton of the hydrogen halide is first added to the oxygen of alcohol to draw the electrons of the nearest carbon atom, but at step two of the reaction the nucleophile attacks this carbon atom, and the intermediate product thus formed eliminates water to preserve the bromine atom:

$$C_2H_5OH \xrightarrow{H^+} C_2H_5O{:}H^+ \xrightarrow{Br^-} \left[CH_3\overset{+}{C}H_2OH_2\right]Br^- \rightarrow C_2H_5Br + H_2O$$

The reaction of the $E1$ type occurs simultaneously. The carbonium ion $CH_3CH_2^+$ is formed, which is then combined with the bromide anion. Ethyl ether and ethylene are formed through this carbonium ion.

* While studying the effect of reagent concentration and the solvent properties on the rate of reaction, it is often possible to state whether the process proceeds according to the kinetic equation of the unimolecular or bimolecular reaction. If so, figures 1 and 2 are used accordingly in the designation of the reaction type. These data are very important for clarification of intricate details of the process. The figures indicate the applicability of the kinetic equation, and not the number of the reacting molecules.

Substitution of the chloride atom for the hydroxyl group by the action of hydrogen chloride on alcohols under the same conditions is slower. Hydrogen iodide reacts with alcohols faster than hydrogen bromide, but the reaction should be carried out under different conditions (Experiments 28 and 29).

Calculating the yield of product. Reactions of organic compounds are usually molecular rather than ionic. They proceed slowly even in a homogeneous medium and with heating. Many reactions are reversible, i.e. they do not proceed to the end but only to the point where the equilibrium between the starting substances and the end products is attained. The reactions very often occur simultaneously in different directions, or the obtained product itself undergoes changes. In both cases, alongside with the main product being synthesized, the by-products of the reaction are accumulated in the reaction medium. The side products are often present in large quantities and interfere with isolation and purification of the main product. For this reason, and also because the main product is inevitably lost in laboratory manipulations, the actual yield of the reaction product is always lower than theoretical, i.e. calculated stoichiometrically from the reaction equation. For convenience of comparison and calculation, the actual yield is expressed in per cent of theory.

Calculate the yield (theoretical and actual) as follows. Write down the reaction equation and underline the substances whose constituents pass into the synthesized product. In our case these are alcohol and potassium bromide. Now put the molecular masses of the substances under their formulas in the equation, and (minding the coefficients) find the weights of these substances in accordance with the equation. In our case one mole (46 g) of alcohol requires one mole (119 g) of potassium bromide. The cheaper substance should be taken in excess to shift the equilibrium in the required direction. Here the mass of the starting alcohol is 2.3 g (3 ml of 96 per cent solution, density 0.78 g/cc, i.e. $3 \times 0.78 \times 0.96$), and that of bromide, 3 g. Alcohol is taken in excess, and calculations should be done with reference to potassium bromide, whose molar quantity is lower. Theoretically, 119 g of potassium bromide must give 109 g of ethyl bromide. Hence 3 g of KBr will give 2.75 g of C_2H_5Br. If the process gives 1.5 g of ethyl bromide, the actual yield is $(1.5 : 2.75) \times 100 = 55$ per cent of theory.

The loss here is mainly caused by volatility of the synthesized product. For small quantities of substances, the loss is relatively higher. The general rule reads that the greater the amounts of reactants, the smaller is the loss from volatility, wetting of the walls, etc. But side products are more likely to form with large starting amounts of the materials, which also reduces the yields.

Calculations of the yield are justified only in cases where pure substances are isolated and weighed, or where the content of the pure substance in the crude material is known.

28
Preparing Methyl Iodide

REAGENTS

Methyl alcohol.
Iodine.
Red phosphorus, dried in a desiccator over concentrated sulphuric acid.

Carry out the synthesis in a round-bottomed flask, having the capacity of 50-100 ml, provided with a two-neck adapter (Fig. 2*f*). Install a long water-cooled reflux condenser into an inclined neck of the adapter and stopper the vertical neck. All joints should be tight.

Place 1.4 g of red phosphorus and 5 g (6.3 ml) of methyl alcohol in the flask. Weigh out, in a test tube, 14 g of iodine ground in a mortar. Place the flask in ice-cold water, connect the reflux condenser, and add iodine through the vertical neck of the adapter in small portions for 15-20 minutes. Close the flask tightly with the stopper after adding each new portion of iodine and shake the flask well. As all iodine has been added, replace the cooling bath by a water bath, heat it to 60-70 °C, and boil the reaction mixture gently.

After 30 minutes cool the flask again and insert another adapter (Fig. 2*e*) connected with a straight-run condenser. Lower the adapter (Fig. 2*d*) of the condenser into a receptacle (almost to the bottom) and place the receptacle in ice-cold water. Heat the flask containing the reaction mixture on a boiling water bath, and distil methyl iodide into the receptacle. Methyl iodide is impure (brown). The yield of the crude product is about 14 g.

To purify the distillate, shake it carefully (to avoid formation of emulsion) with dilute alkali solution until the distillate is decolourized; then shake with water, and separate the lower layer into a test tube provided with a side arm. Add a piece of anhydrous calcium chloride and a boiling stone, connect a 'cold finger' condenser to a cooled (to 0 °C) receptacle (Fig. 3), and distil the pure product on a water bath. Almost all methyl iodide will be distilled at 40-41 °C. The yield is 12-13 g.

Freshly distilled methyl iodide is colourless. To prevent it from colouring in storage, add a small drop of mercury, stopper the bottle tightly, and keep under water.

29
Preparing Ethyl Iodide

REAGENTS

Ethyl alcohol, rectified.
Iodine.
Red phosphorus, dried in a desiccator over concentrated sulphuric acid.

Proceed as instructed in the previous experiment. Place 5 g (6.5 ml) of alcohol in a reaction flask, and add 1.4 g of phosphorus and 14 g of iodine. Boil the mixture with a reflux condenser on a water bath at a temperature of 90-100 °C. To distil the product, remove the flask from the bath and heat over a burner. The yield of crude product is about 14 g and of pure product, 12-13 g. The pure product distils at 69-71 °C.

Alkyl iodides are produced by the action of hydrogen iodide on alcohols. The process is easier than that with alkyl bromides. The reaction proceeds according to the equation:

$$ROH + HI \rightleftharpoons H_2O + RI$$

But hydrogen iodide cannot be obtained by the reaction of iodides with concentrated sulphuric acid, since the latter oxidizes hydrogen iodide to free iodine. Phosphorus triiodide is therefore used to substitute the iodine atom for the hydroxyl group; the triiodide is readily formed by the reaction of iodine and phosphorus:

$$2P + 3I_2 \rightarrow 2PI_3$$

$$PI_3 + 3ROH \rightarrow H_3PO_3 + 3RI$$

The reactions by which methyl iodide and ethyl iodide are produced are probably the bimolecular nucleophilic substitution type (S_N2).

Alkyl chlorides and bromides are often prepared by a similar method—by the action of phosphorus trichloride or tribromide on alcohols.

If alcohol contains water (Experiment 39), it hydrolyses phosphorus iodide and the formed hydrogen iodide partly reacts with alcohol, and partly evaporates.

Traces of iodine, which colour alkyl iodides, can be removed by the action of aqueous alkali solution:

$$I_2 + 2NaOH \rightarrow NaI + NaOI + H_2O$$

To bind iodine that is liberated during storage of alkyl iodides and colours them, metallic mercury should be added. The reagent should be kept in the dark.

Halogen derivatives of hydrocarbons have specific odour and are insoluble in water. The density of a substance obtained by substitution of halogen for hydroxyl is normally higher than that of the starting substance.

30
Preparing Ethylene Bromide (Dibromoethane)

REAGENTS

Ethyl alcohol, rectified or crude.
Sand, white quartz, dry.
Bromine.

Use the HOOD.

Prepare ethylene as instructed in Experiment 24, except that use a 150-200 ml round-bottomed flask instead of a test tube.

Close the flask with a plug through which a soda lime tube is passed. Connect the latter with a long glass tube drawn at one end and having a small bulb in the middle. Insert this tube into a stopper, closing the receptacle provided with a tubulure, so that it almost reaches the bottom of the receptacle. Connect another soda lime tube to the tubulure.

Place 10 ml of alcohol in the flask, add carefully 25 ml of concentrated sulphuric acid and 4-5 g of dry sand. Place 1 ml of water in the receptacle and then add 2 ml of bromine (from a graduated pipette).

Close the receptacle tightly with the stopper through which ethylene delivery tube is passed, and place it into a beaker containing cold water. Heat the flask first very gently, then more intensively. Regulate heating so that the current of ethylene is quiet and uniform and that the foam does not rise to the neck level. Liquid from the receptacle can slightly rise into the tube but it will not pass further than the bulb.

At the beginning of ethylene passage through bromine, the vapour of the latter is partly carried with the gas current to colour the first portions of soda lime in the tube. In 10-15 minutes the colour of bromine vapour over the liquid vanishes and the reaction is stopped. Transfer the heavy red oil from the receptacle into another vessel, shake with dilute alkali solution to decolourize it, then wash with water, allow to stand, pipette (Experiment 3) into a dry test tube, and use for the experiments.

To purify the obtained ethylene bromide, dry it with calcium chloride with slightly heating, transfer into a test tube with a side arm, and distil with a thermometer. The product is almost all distilled at 129-131 °C. The yield is 6-6.5 g.

Formation of ethylene has been described above (Experiment 24). In this experiment the volume of the reaction mixture is larger and in order to ensure a smooth process, a catalyst (quartz sand) should be added. It will accelerate the thermic decomposition of ethylsulphuric acid (see Experiments 41 and 43).

For bromination of hydrocarbons across the double bond see Experiment 18.

31
Elimination of Halogen by Alkali

REAGENTS

Halogen derivatives (see Table 2).
Alkali, dilute solution free from halide ions.

Carry out parallel experiments with several different halogen derivatives of hydrocarbons.

Shake 0.5 ml of each halogen derivative separately in test tubes with 2-3 ml of distilled water, allow to settle, and transfer the greater part of the aqueous layer into another test tube. Add a few drops of silver nitrate and test the mixture for the presence of halide ion. If $AgNO_3$ produces a precipitate, wash the halogen derivative with new portions of distilled water once or twice and test for the halide ion again.* Now add 1-2 ml of alkali solution to the remaining water and the halogen derivative in the first test tube and heat carefully with shaking until the mixture starts boiling. To prevent too rapid evaporation of the halogen derivative, heat slowly, and begin with the upper layer of the liquid. Allow the mixture to cool, settle, and transfer part of the water-alkali layer into another vessel. Acidify it with dilute nitric acid and add a few drops of silver nitrate.

The difference in mobility of the halogen atoms in the compounds under study shows in the different quantities of precipitated silver halides.

Mobility of the halogen atom bonded to carbon can be different. In most organic halogen derivatives the bond is not ionogenic and the halogen is slowly eliminated by hydrolysis with water or even alkali. In compounds of similar type of bonding, iodine atom is usually bonded weaker than bromine atom, and bromine atom is more mobile than chlorine atom. In halogen derivatives of saturated hydrocarbons, the bond of halogen with the primary carbon atom is the strongest, and with the tertiary, the weakest. The halogen united to the double-bonded carbon is not mobile. On the contrary,

* Impure halogen derivatives often contain free hydrohalic acid that can be removed by washing with water. If the halogen bond is not strong, halide ion cannot be eliminated even after multiple washings with water.

the double bond of the neighbouring carbon atom significantly increases mobility of the halogen atom.

Accumulation of halogen atoms in a molecule of an organic substance can produce different effect on the easiness with which they can be eliminated (cf. Experiments 32-35).

The reaction of halogen derivatives with water or aqueous alkali solution is mainly the substitution of hydroxyl group for halogen:

$$RX + H_2O \rightarrow ROH + HX$$

$$RX + NaOH \rightarrow ROH + NaX$$

Replacement of halogen by hydroxyl is the reaction reverse to the formation of halogen derivative from alcohols and it proceeds by a similar pattern (see explanations to Experiment 27).

Alkali solution in alcohol reacts with halogen derivatives more energetically, since unlike water, alcohol well dissolves halogen derivatives, and alkali is more active in alcoholic solution than in water (see explanations to Experiment 40). Unsaturated compounds are predominantly formed in this case, i.e. hydrogen halide molecule is eliminated.

Methyl alcohol is a suitable solvent for alkali. Alkali solutions in ethyl alcohol quickly turn brown owing to resinification of alcohol.

32
Elimination of Halogen by Silver Nitrate Solution in Alcohol

REAGENTS

Halogen derivatives.

Silver nitrate, 4 per cent saturated solution in ethyl alcohol.

Carry out the experiment with several different halogen derivatives. Wash them before the experiment with water to remove impurities (see Experiment 31).

Place 1-2 ml of silver nitrate in a dry test tube and add a drop of a halogen derivative. If silver halide does not precipitate within 1-2 minutes, heat the solution to boiling, cool, and observe again.

Silver nitrate solution in alcohol is a suitable reagent for eliminating halogen, since the process occurs in a homogeneous medium. The halogen atom is replaced by the ONO_2 group to form an ester of nitric acid, alkyl nitrate:

$$RX + AgONO_2 \rightarrow AgX\downarrow + RONO_2$$

Other reactions occurring simultaneously, also precipitate silver halide, and its quantity usually characterizes the relative mobility of halogen atom in the original substance.

Tertiary halogen derivatives of saturated hydrocarbons give off the halogen, under the action of this reagent, at room temperature, and the secondary and primary derivatives, on heating. Some chlorine substituted compounds, e.g. dichloroethane and chloroform, react very slowly. On the contrary, carbon tetrachloride reacts very quickly with heating. It should be noted that carbon tetrachloride is more stable to aqueous solution of alkali than chloroform (cf. Experiment 35).

Silver nitrate solution in alcohol can produce precipitate in the absence of halogen. To illustrate, many unsaturated compounds give sparingly soluble products of silver nitrate addition, and some organic acids produce sparingly soluble silver salts. But unlike silver halide precipitates, they are dissolved if nitric acid is added.

33
Elimination of Halogen by Sodium in Alcohol Solution (Stepanov's Method)

REAGENTS

Halogen derivatives.
Ethyl alcohol, rectified.
Sodium metal.

Dissolve 3-4 drops of a halogen derivative in 2-3 ml of alcohol and add a pellet of sodium metal (the size of a little peaseed), cleaned from crust and dried in filter paper. The mixture soon begins boiling. To cool it, immerse the test tube in water. Put a flame (a burner or a splint) to the mouth of the test tube to check for liberation of hydrogen. A mixture of hydrogen with air produces a specific slight blow. The liquid in the test tube usually becomes cloudy, or a halide that is sparingly soluble in alcohol precipitates. The solution can sometimes turn yellow or brown.

As hydrogen bubbles stop evolving, check to see that all sodium is dissolved. If so, add 3-4 ml of distilled water and diluted nitric acid (until the solution reacts acid). Now add a few drops of silver nitrate: ample precipitate of silver halide falls out.

The method was developed in 1905 by A. V. Stepanov. It can also be used for quantitative determination of halogens in organic compounds. To do so, the test substance is weighed accurately, treated as described above to eliminate halogen, acidified with nitric acid, and titrated with $AgNO_3$.

The rapidity and completeness of halogen atom elimination in these conditions are explained by simultaneous action on halogen derivatives (in a homogeneous medium) of sodium alcoholate and nascent hydrogen:

$$Na + C_2H_5OH \rightarrow C_2H_5ONa + H$$

$$RX + 2H \rightarrow RH + HX$$

$$RX + C_2H_5ONa \rightarrow ROC_2H_5 + NaX$$

Side reactions occur simultaneously. They often produce resinous substances and colour the liquid.

Some halogen derivatives, for example, compounds containing a halogen attached to the carbon atom of the aromatic nucleus, fail to eliminate the halogen completely even in these rigid conditions.

The general method of reducing organic compounds with sodium in alcoholic solution was discovered by A. N. Vyshnegradsky.

34
Formation of Ethylene from Ethylene Bromide

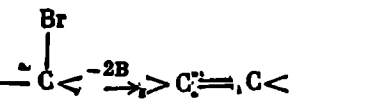
REAGENTS

Ethylene bromide.
Ethyl alcohol, crude or rectified.
Zinc, granules.

Place about 1 ml of ethylene bromide, an equal volume of alcohol, and 1-2 grains of zinc in a test tube with a side arm and provided with a stopper. Connect a glass tube with a drawn end to the side arm.

Heat the mixture until it starts boiling. Remove the burner. If bubbling stops, heat the mixture slightly again. Soon quiet liberation of gas is renewed. Immerse the end of the gas outlet tube into test tubes containing the corresponding reagents and make sure that the liberated gas is an unsaturated compound. Light the gas at the drawn end and put a porcelain dish into the flame (see Experiment 24).

Elimination of two halogen atoms attached to the neighbouring carbon atoms results in the formation of the double bond:



Zinc metal is often used to eliminate halogen; like in other similar cases, the intermediate products of this reaction are organozinc

compounds, which were first studied by A. M. Butlerov and later by A. M. Zaitsev and S. N. Reformatsky.

The method of obtaining ethylene by the action of zinc on ethylene bromide in alcohol was discovered by A. P. Sabaneev in 1877. This reaction, as applied to dibromides of more complicate structure, was studied by N. J. Demianov and A. E. Uspensky.

Any homologue of ethyl alcohol can be used in this experiment. The reaction can be essentially accelerated by adding a few drops of copper sulphate solution to the reaction mixture. Copper is liberated on the surface of zinc to form a copper-zinc couple that binds halogen atoms more energetically. Dichloroethane reacts with zinc much slower than dibromoethane. In similar conditions, methane is formed from chloroform or methyl iodide, and ethane from ethyl iodide.

35
Reaction of Chloroform and Carbon Tetrachloride with Alkali

REAGENTS

Chloroform.
Carbon tetrachloride.

Place a few drops of chloroform and 2-3 ml of dilute alkali solution in a test tube, gently heat for 1-2 minutes with jolting until chloroform starts boiling, and cool the test tube in water. Decant the obtained alkaline solution from the chloroform residue if any, and divide into three parts.

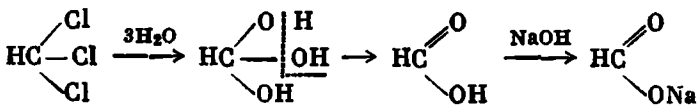
A. Add dilute nitric acid to one portion of the hydrolysate until it reacts acid, and then a few drops of silver nitrate solution.

B. Add concentrated aqueous ammonia by drops to 1 ml of silver nitrate (in a separate test tube) to dissolve silver oxide that first precipitates. Add the solution thus obtained to the second portion of the hydrolysate.

C. Add a few drops of potassium permanganate to the third hydrolysate portion. Observe the changes.

Repeat the experiment using carbon tetrachloride instead of chloroform.

Chloroform is quickly hydrolysed in an alkaline medium to form a salt of formic acid:



or

$$CHCl_3 + 4NaOH = 3NaCl + 2H_2O + HCOONa$$

It can be seen that the halogen that was bound with carbon is passed into the aqueous solution as ion (portion A). The intermediate product of the alkaline hydrolysis of chloroform is probably an unstable derivative of divalent carbon, dichlorocarbene, $\rangle CCl_2$, which is then hydrolysed to join water.

Chloroform does not undergo hydrolysis in water, i.e. in a neutral medium.

Formation of the carboxyl group during hydrolysis is characteristic of halogen derivatives having three halogen atoms bonded to one carbon atom.

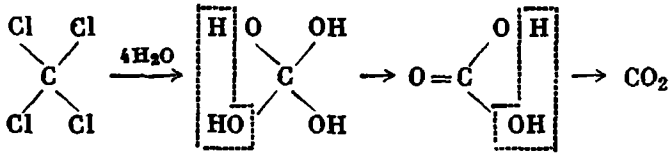
Being an aldehyde, formic acid is readily oxidized to carbonic acid to reduce, for instance, silver oxide in ammonia solution to silver metal (portion B).

Potassium permanganate oxidizes formic acid in an alkaline solution to form a bright green manganate (portion C):

$$2KMnO_4 + 3NaOH + HCOONa = K_2MnO_4 + Na_2MnO_4 + 2H_2O + Na_2CO_3$$

The solution first darkens to mark the moment of simultaneuos presence in solution of MnO_4^- (violet-red) and MnO_4^{2-} (green) ions; the solution absorbs almost in the entire visible region of the spectrum.

Unlike chloroform, carbon tetrachloride almost completely fails to hydrolyse in the conditions of this experiment. When hydrolysed in more rigid conditions, it produces carbonic acid:



which, in contrast to formic acid, is not a reductant.

36
Preparing Bromoform

REAGENTS

Acetone.
Bromine.

USE A HOOD.

Mix 2 ml of acetone and 4 ml of dilute alkali solution in a test tube and add 10-15 drops of bromine. Shake the contents: the mix-

ture becomes hot and cloudy. The colour quickly vanishes and heavy drops of bromoform sink to the bottom of the test tube. Take the bromoform by a pipette and use in the experiments. To purify the bromoform, dry it with a piece of calcium chloride, transfer to a test tube with a side arm, and distil.

The obtained product is hydrolysed with aqueous solution of alkali, with boiling, faster than chloroform and gives all specific reactions of the latter (see Experiment 35).

Acetone readily reacts with bromine (see Experiment 69) to form, among bromination products, tribromoacetone:

$$CH_3COCH_3 + 3Br_2 \longrightarrow CBr_3COCH_3 + 3HBr$$

Alkali splits tribromoacetone into bromoform and an acetate

$$CBr_3 - \overset{|}{\underset{|}{}} COCH_3 + H - \overset{|}{\underset{|}{}} ONa \longrightarrow CHBr_3 + CH_3COONa$$

The obtained bromoform contains admixture of carbon tetrabromide, CBr_4 (m. p. 94 °C).

37
Preparing Iodoform

REAGENTS

Ethyl alcohol, rectified or crude.
Iodine, crystalline.

Place 1 g of iodine and 1 ml of alcohol in a small beaker and shake. Add 10 ml of water: iodine precipitates from the alcoholic solution. Add a dilute alkali solution, drop by drop, with shaking and heating gently to 60-70 °C, until the crystals of iodine disappear. The moment is attained very soon. Pale yellow iodoform begins simultaneously precipitating from the liquid.

Allow the warm mixture to stand for 5-10 minutes, then cool, suck off the precipitate on a funnel with a disc and dry the obtained iodoform on a filter paper. The yield is close to theoretical. Purify iodoform by re-crystallizing from acetone or alcohol. Iodoform has a characteristic, penetrating odour. When heated over the melting point it readily decomposes with liberation of free iodine.

The formation of iodoform in the conditions of the experiment can be expressed by the following equation:

$$C_2H_5OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCOONa + 5NaI + 5H_2O$$

Experiment 49 gives a detailed description of this process.

Iodoform is quickly hydrolysed by an aqueous solution of alkali with heating and it gives the same specific reactions as chloroform (see Experiment 35).

CHAPTER SIX

ALCOHOLS. ETHERS. ESTERS OF MINERAL ACIDS

Alcohols used in the experiments described in this chapter should be kept ready for use. Almost all of them (see Table 3) are readily accessible. Ethylsulphuric acid, ethyl ether, ethyl nitrite, and alkyl borates should be prepared in the course of the experiments.

Table 3

Properties of Alcohols and Their Derivatives

Substance	Formula	M. p., °C	B. p., °C	Density, g/cc
Methyl alcohol	CH_3OH	—98	65	0.79
Ethyl alcohol	C_2H_5OH	—117	78	0.79
n-Propyl alcohol	$CH_3CH_2CH_2OH$	—127	97	0.80
Isopropyl alcohol	$(CH_3)_2CHOH$	—88	82	0.79
n-Butyl alcohol	$CH_3(CH_2)_3CH_2OH$	—89	118	0.81
Isobutyl alcohol	$(CH_3)_2CHCH_2OH$	—108	108	0.80
n-Amyl alcohol	$CH_3(CH_2)_3CH_2OH$	—78	138	0.81
Isoamyl alcohol	$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!\diagdown\!\!\diagup CHCH_2CH_2OH$	—117	131	0.81
Ethylene glycol	$CH_2(OH)CH_2OH$	—12	197	1.11
Glycerol	$CH_2(OH)CH(OH)CH_2OH$	19	290 with decompos.	1.26
Mannitol	$CH_2(OH)(CHOH)_4CH_2OH$	166	—	1.49
Ethyl ether	$C_2H_5OC_2H_5$	—116	35	0.71
Ethylsulphuric acid	$C_2H_5OSO_2OH$	—	decomposes	1.32
Ethyl nitrite	C_2H_5ONO	—	17	0.90
Trimethyl borate	$(CH_3O)_3B$	—	65	0.92
Ethyl borate	$(C_2H_5O)_3B$	—	118	0.87

Both rectified and crude ethyl alcohol can be used in most experiments unless special requirement for the rectificate is emphasized. Fusel oil can be used instead of isoamyl alcohol.

Monohydric alcohols containing less than four carbon atoms in the molecule are readily miscible with water in any proportion. As the carbon chain grows in length the solubility of monohydric alcohols quickly decreases and solubility markedly increases with growing number of hydroxyl groups in the molecule. Ethylene glycol and glycerol are miscible with water in any proportion.

Ethers are less readily soluble in water than the corresponding alcohols.

The relatively high boiling points of alcohols are explained by the association of their molecules with formation of the hydrogen bonds (like in liquid water). Ethers have no hydroxyl hydrogen atom and their boiling points are therefore markedly lower than those of alcohols having the same number of carbon atoms.

38
Salting Out of Alcohol from Its Aqueous Solution

REAGENTS

Ethyl alcohol, rectified.

Potassium carbonate, powder, or *sodium thiosulphate*, crystals.

Mix 2 ml of ethyl alcohol with 2 ml of water having the same (room) temperature. Watch the thermometer to note the rise of temperature as alcohol is mixed with water.

Place a few drops of the alcohol solution thus obtained, having the concentration of about 50 per cent, onto a glass plate and try to light it up.

Add about 2 g of potassium carbonate (or sodium thiosulphate), shake, and allow to settle. The supernatant layer that soon forms above the salt solution is alcohol. Try it with fire again.

As alcohol is mixed with water, the solution becomes hot and its volume decreases because of the hydration process. The presence of hydrates in water-alcohol mixtures was established by D. I. Mendeleev by physicochemical analysis, as he studied densities of these mixtures.

Mixtures containing much water are incombustible, and only produce inflammable vapour when heated.

Upon addition of mineral salts that are sufficiently well dissolved and hydrated in water a considerable part of water is bonded to reduce hydration and solubility of alcohol. Alcohol that is liberated

in the salting-out process still contains to 10 per cent of water, but it can burn.

39
Detection of Water in Alcohol and Dehydration of Alcohol

REAGENTS

Ethyl alcohol, rectified.
Copper sulphate, $CuSO_4 \cdot 5H_2O$, powder.

Heat 1.5-2 g of $CuSO_4 \cdot 5H_2O$ in a porcelain dish or a crucible over a burner with stirring the salt by a copper wire until the blue colour fully vanishes and water vapour stops evolving. Allow the white powder to cool, transfer it to a dry test tube, and add 2-3 ml of ethyl alcohol. Shake the test tube over a slow flame: the white powder soon turns blue.

Decant carefully the dehydrated alcohol thus obtained and keep for use in Experiment 40.

Pure alcohols often contain traces of dissolved water. Common rectified ethyl alcohol contains about 5 per cent of water that fails to be removed by ordinary fractionation, since rectified alcohol is an *azeotropic* mixture (see explanations to Experiment 5). Readily hydrated substances, such as calcium oxide, anhydrous copper sulphate (see explanations to Experiment 3) bind water in alcohol, and distillation of alcohol containing such salts produces anhydrous, or *absolute*, alcohol.

Blue vitriol, dehydrated by calcining, binds water to convert into a blue crystal hydrate $CuSO_4 \cdot 5H_2O$. The change of colour is indicative of the presence of water in alcohol and the dehydration process or of other organic liquids that do not dissolve blue vitriol. Excessively calcined blue vitriol is hydrated slowly. Anhydrous calcium chloride is not suitable for dehydration of alcohols since it forms crystal alcoholates with many of them. Concentrated sulphuric acid cannot be used for the purpose either (see Experiment 41).

Absolute alcohols are as a rule very hygroscopic, and since synthesis of many substances requires the absence of even traces of water, small quantities of sodium are added to absolute alcohols (see Experiment 40) and the latter are then separated from the alkali and alcoholate by distillation.

Anhydrous ethyl alcohol was first obtained by the Russian scientist T. E. Lovits.

40
Formation and Hydrolysis of Alcoholate

REAGENTS

Ethyl alcohol, dehydrated (see Experiment 39).
Sodium metal.

Decant carefully the anhydrous ethyl alcohol prepared in Experiment 39 into a dry test tube. Cut out a piece of sodium (the size of a pea), separate it from crust and traces of kerosene, and add to the alcohol. To preclude excess heating and boiling out of alcohol, cool the test tube in water in a beaker. When the liberation of gas becomes quiet, put the mouth of the test tube to the flame of a burner: the liberating hydrogen mixes with air to form an explosive mixture that inflames with a characteristic blast.

The liquid gradually thickens, sodium becomes coated with solid alcoholate, and the reaction is so retarded that the test tube should be heated. If hydrogen almost stops evolving while sodium still remains non-dissolved, heat the mixture to make it fluid, and remove the remaining sodium using a wire. Place the sodium into the bottle intended for sodium wastes (see Chapters 1 and 2).

As the concentrated solution of the alcoholate thus obtained cools, it crystallizes.

Add 5-6 ml of water into the test tube and test the reaction with phenolphthalein.

The reaction of sodium with alcohols, with formation of sodium alcoholates, proceeds as this:

$$2ROH + 2Na \longrightarrow 2RONa + H_2$$

Substitution of sodium for hydrogen is characteristic of organic substances containing the hydroxyl group in its molecule. The reaction is exothermic but less vigorous than that of sodium with water. The reagents used in this reaction should therefore be dry. The reaction of sodium with secondary and tertiary alcohols is slower than with primary alcohols. If insufficient quantities of sodium are taken for the reaction, the alcoholate fails to be liberated from the solution. It can be precipitated by adding approximately an equal volume of dry ethyl ether. Solid or viscous alcohols should first be dissolved in anhydrous ether or any other liquid inactive towards sodium. The reaction is much slower in this case.

Free acids react with sodium much more energetically than alcohols to form the corresponding salts.

Besides compounds having hydroxyl groups, mercaptans and secondary amines, as well as some aldehydes, ketones, esters, and

acid amides can also liberate hydrogen by the action of sodium metal. Some compounds having hydroxyl groups, e.g. resorcinol, $C_6H_4(OH)_2$, salicylic acid, $C_6H_4(OH)COOH$, do not produce vivid reaction with sodium.

Sodium alcoholates, crystalline salt-like substances, readily undergo hydrolysis to give the starting alcohol and free alkali:

$$RONa + H_2O \longrightarrow ROH + NaOH$$

Crystalline sodium ethylate that is liberated in the experiment contains alcohol of crystallization and has the following composition: $C_2H_5ONa \cdot 3C_2H_5OH$.

Alcoholates of other alkali metals are formed in a similar way. Alcoholate molecules contain a strongly polar bond, O—metal, and in alcohol solutions they form ions of metal and of alkoxyl, $R—O^-$. The constants of alcohol ionization with the formation of hydrogen ions are one or two orders of magnitude lower than that of water. For this reason, alcoholates of alkali metals are stronger bases than caustic alkalis, and they more readily bind hydrogen ion to form alcohols. Because of the reversible character of the reaction of alkali with solvent (alcohol), the alcoholic solution of NaOH or KOH contains a certain quantity of alcoholate and has stronger alkaline properties than the aqueous solution of the same alkali (see explanations to Experiment 31).

Alcoholates of the alkaline earth metals and of aluminium are obtained by other methods. Aluminium alcoholates, $Al(OR)_3$, studied in detail by V. E. Tishchenko, are distilled without decomposition and can be regarded as esters of aluminium hydroxide having acid properties.

High reactivity of alcoholates accounts for their wide use in various syntheses.

41
Formation of Ethylsulphuric Acid and Its Properties

REAGENTS

Ethyl alcohol.
Barium carbonate, powder.

To 1 ml of ethyl alcohol, carefully add, in small portions, with shaking, 1 ml of concentrated sulphuric acid. Heat the hot mixture in hot water for 2-3 minutes and then cool. Transfer the solution into a beaker or a dish containing 25 ml of cold water, and add, in small portions, 5 g of barium carbonate powder with constant stirring.

The mixture foams strongly. As soon as barium carbonate is all added, and liberation of carbon dioxide stops, try the mixture with litmus: the reaction must be neutral. Heat the obtained thick mixture on a boiling water bath and separate part of liquid on a dense filtre. Place 2-3 ml of the liquid into three test tubes.

A. Evaporate one portion of the filtrate to dryness in a porcelain dish or in a crucible. When calcined gently, the white residue chars.

B. Acidify the second portion of the filtrate with dilute sulphuric acid: sodium sulphate precipitates immediately. It is insoluble in acids.

C. Add 0.5-1 ml of concentrated hydrochloric acid to the third portion of the filtrate and heat the clear acid solution on a boiling water bath. The liquid soon becomes cloudy and barium sulphate precipitates in a few minutes.

If the acidified filtrate is allowed to stand at room temperature, barium sulphate will precipitate only in a few days.

42
Reaction of Isoamyl Alcohol with Sulphuric Acid

REAGENTS

Isoamyl alcohol.

Place 4 ml of cold concentrated sulphuric acid into a test tube and add carefully, in small portions, 2 ml of isoamyl alcohol. Shake the mixture at short intervals and cool the test tube in water, preferably ice-cold water. As soon as the alcohol is all added, allow the obtained homogeneous, almost odourless liquid to stand for 3-5 minutes, and then divide into two portions.

A. Gradually mix one portion of the solution with 5-7 ml of cold water with shaking and cooling in a test tube. The formed solution is clear and odourless whereas the starting alcohol is sparingly soluble in water and has specific odour.

If the solution was allowed to get hot in the process of mixing the alcohol with the acid, the resultant solution is slightly cloudy and the odour of diisoamyl ether can be sensed, but an insoluble layer is not formed.

B. Heat the other portion of the solution almost to boiling for 2-3 minutes: the liquid becomes brown and small bubbles of gas are liberated. The odour of the gas is that of sulphur dioxide. Cool the liquid, and transfer carefully into a test tube containing water. A layer of diisoamyl ether, insoluble in water, is formed.

43
Formation of Ethyl Ether

REAGENTS

Ethyl alcohol.
Sodium carbonate, saturated solution.

A. Mix 1 ml of ethyl ether and 1 ml of concentrated sulphuric acid in a test tube (see Experiment 41). Heat carefully the hot mixture over a burner until it starts boiling: combustible vapours are not formed, nor can the odour of the ether be felt. Put the test tube away from the burner and add carefully 5-10 drops of the alcohol: the odour of the ether can be smelt immediately. Heat the mixture again and light up the ether vapour. Note the differences in the appearance of the ether and alcohol flames.

B. If some quantity of ether is to be isolated, mix similarly 5 ml of alcohol with 4 ml of concentrated sulphuric acid. Add a boiling stone, close the test tube with a stopper provided with a gas outlet tube, connect a condenser, and distil 2-3 ml into a receptacle placed in a beaker with cold water. See to it that during distillation there should be no open flame or a hotplate in the vicinity. Add three volumes of saturated soda solution to the distillate and shake the receptacle. Collect the supernatant ether by a pipette. Test the obtained ether for inflammability and volatility. Use the ether in Experiments 52 and 53.

As primary alcohols react with concentrated sulphuric acid, an acid ester, i.e. ethylsulphuric acid, is first produced

$$ROH + HOSO_2OH \rightleftharpoons ROSO_2OH + H_2O$$

Esterification reactions are discussed in more detail in explanation to Experiments 93-95.

The formation of alkylsulphuric acid is an exothermic reaction and it is reversible.

In the free state, alkylsulphuric acids are thick liquids readily soluble in water. They are strong and form stable salts. Unlike calcium sulphate and barium sulphate, calcium and barium salts of alkylsulphuric acids are readily soluble in water.

Hydrolysis of alkylsulphuric acids in aqueous solutions proceeds by the equation reverse of that by which they are formed, i.e. free sulphuric acid and the corresponding alcohol are liberated. Experiment 41 shows that hydrolysis occurs at room temperature (20 °C) but the process is very slow and can be detected only in a few days, whereas at a temperature of 100 °C it takes only a few minutes. The rate of hydrolysis at 100 °C is thus 1500 times higher. The temperature coefficient of this reaction can be assessed approximately from

these data. As the temperature rises by 80 °C, the rate of the reaction is accelerated 1500 times. The temperature coefficient (the relative acceleration of the reaction rate per each 10 °C) is therefore $\sqrt[8]{1500}$, i.e. about 2.5.

Excess quantities of alcohol act on alkylsulphuric acids (with heating to 130-140 °C) like water: sulphuric acid is recovered and ether is liberated:

$$RO\boxed{SO_2OH+HO}R' \longrightarrow ROR'+H_2SO_4$$

Ethers are more volatile than alcohols having the same hydrocarbon radicals, and they are less reactive.

When strongly heated (better in vacuum), alkylsulphuric acids are decomposed to eliminate sulphuric acid in the absence of excess alcohol as well. Lower homologues can give the corresponding neutral esters, the product of reaction of two molecules:

$$RO\boxed{SO_2OH+HO}SO_2OR \longrightarrow SO_2(OR)_2+H_2SO_4$$

The formed dialkyl sulphates are neutral. They are widely used as alkylating agents, since the bond R—O, in contrast to the similar bond in the molecules of carboxylic acid esters (see explanations to Experiments 93-95), is readily broken. But it is only methylsulphuric acid that gives good yields of diethyl sulphate. When heated, other alkylsulphuric acids decompose with the formation of the corresponding alkene and sulphuric acid (see Experiments 24 and 27):

$$C_nH_{2n+1}OSO_2OH \longrightarrow C_nH_{2n}+H_2SO_4$$

Here, in the reaction of sulphuric acid with alcohol on strong heating (170 °C and over), a molecule of water is eliminated from the alcohol molecule, i.e. sulphuric acid acts as a dehydrating agent, like in the formation of ether. Sulphuric acid also acts as an oxidant on organic compounds with the formation of sulphur dioxide. Diisoamyl ether, $(C_5H_{11})_2O$, formed in Experiment 42, B, therefore contains also pentene polymers (see Experiment 21) and brown products of oxidation and condensation.

The reaction between sulphuric acid and higher primary alcohols gives mostly unsaturated hydrocarbons and only small amounts of ethers. Secondary and tertiary alcohols do not form stable alkylsulphuric acids in these conditions but are immediately dehydrated.

Charring on ignition (Experiment 41, A) indicates the presence in solution of a non-volatile organic substance (cf. Experiment 14). Precipitation of $BaSO_4$ (Experiment 41, B) indicates the presence in solution of barium ion, and hence, the absence of sulphate ion.

Precipitation of $BaSO_4$ on heating with HCl indicates the formation of sulphuric acid by gradual hydrolysis of ethylsulphuric acid.

The percentage of carbon in a molecule of ethyl ether is much higher than in ethyl alcohol molecule. The flame of the ether (in contrast to that of alcohol) is therefore luminous.

44
Detection of Peroxides in Ethyl Ether

REAGENTS

Ethyl ether, pure, pharmacopeal.
Ethyl ether, crude, or long kept in storage.
Sodium thiosulphate, very dilute solution.
Mohr's salt, fresh 2 per cent solution.
Ammonium thiocyanate, or *potassium thiocyanate*, 1 per sent solution.

Carry out parallel experiments with pure and crude ether.

A. Add 2-3 drops of sulphuric acid to 1 ml of potassium iodide solution. If the liquid turns yellow, decolourize it by adding sodium thiosulphate (avoid excess thiosulphate). Add 1 ml of the ether to the colourless acid solution, shake vigorously, and allow to stand.

B. Add a few drops of thiocyanate to 1 ml of Mohr's salt. Next add 1 ml of the ether to the colourless liquid and shake energetically.

In a few minutes, compare the colour of the ether layers in the test tubes in Experiment A with that of the water layers in the test tubes of Experiment B.

When kept in air for a long time (especially exposed to light), ether is partly oxidized to form organic derivatives of hydrogen peroxide, mostly hydroxyethyl peroxide. In the presence of water the latter falls into hydroxyethyl hydroperoxide and acetaldehyde:

$$(C_2H_5)_2O + 3O \longrightarrow CH_3CH(OH)-O-O-CH(OH)CH_3 \xrightarrow{+H_2O}$$
$$\longrightarrow CH_3CH(OH)-O-OH + CH_3CHO$$

Organic peroxides and hydroperoxides are strong oxidants. They liberate iodine from acidified potassium iodide solution:

$$2HI + O = H_2O + I_2$$

and oxidize ferrous salts to ferric salts that react with thiocyanates to form brightly coloured ferric thiocyanate (cf. Experiment 53). Iodine is readily soluble in ether and ferric thiocyanate, in water. Many ferrous salts are readily oxidized by atmospheric oxygen to give the thiocyanate colour in the absence of other oxidants as well. The double salt ferrous ammonium sulphate (Mohr's salt,

$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$) is more stable and hence more convenient for use in this experiment.

The presence of aldehyde can be detected by the reaction with Schiff's reagent (see Experiment 61).

If ether was kept for a long time and has become rich in peroxides, it can produce a heavy blast at the end of distillation. To remove peroxides, shake the ether with an acidified solution of green vitriol.

The use of organic peroxides for syntheses and analyses has been studied in detail by N. A. Prilezhaev, and later by S. S. Nametkin. Organic peroxides are widely used as catalysts in the manufacture of some important polymers (see Chapter 20).

The formation of organic peroxides is of special importance in ombustion of fuels, e.g. in automobile and aviation engines.

45
Oxidation of Ethyl Alcohol with Chromic-Sulphuric Acid

REAGENTS

Ethyl alcohol.
Potassium dichromate, 5 per cent solution.

Mix 2 ml of potassium dichromate in a test tube with 1 ml of dilute sulphuric acid and 0.5 ml of ethyl alcohol. Heat the mixture gently. The oxidation process shows itself by the change in colour of the solution, and the formation of acetaldehyde, by the characteristic odour.

Formation of acetaldehyde by this method (in solution) is described in more detail in Experiment 56.

46
Oxidation of Isoamyl Alcohol with Chromic-Sulphuric Acid

REAGENTS

Isoamyl alcohol.
Potassium dichromate, powder.

Add about 0.5 g of powdered potassium dichromate to a mixture of 6 drops of concentrated sulphuric acid and 3 drops of isoamyl alcohol. Shake the mixture and add 0.5 ml of water. Heat the mixture: the colour changes and a sweetish, apple-like odour of isovaleric aldehyde appears. As heating is continued, a disagreeable odour (rotten cheese) of isovaleric acid can be smelt.

47
Oxidation of Ethyl Alcohol with Potassium Permanganate

REAGENTS

Ethyl alcohol.
Potassium permanganate, crystals.

Place 0.5 g of potassium permanganate, 3 ml of water, and 0.5 ml of ethyl alcohol into a test tube provided with a stopper and an outlet tube. On slightly heating, a vigorous reaction begins. Cool the test tube in a beaker with water. Then heat carefully again and boil for 1-2 minutes. Add 3 ml of dilute sulphuric acid, drop a boiling stone, connect the outlet tube, and distil about 0.5 ml into a receptacle. Note the odour of the distillate and its reaction to litmus. Test a sample of the distillate for the specific reaction for acetic acid (with ferric chloride; cf. Experiment 84).

48
Detection of Methyl Alcohol in Ethyl Alcohol

REAGENTS

Ethyl alcohol, pure.
Ethyl alcohol, containing 3-5 per cent of methyl alcohol.
Sodium (potassium) sulphite, neutral or acid, powder or solution.
Schiff's reagent, solution (see Experiment 61).

Carry out parallel experiments, one with pure ethyl alcohol and the other with alcohol containing admixture of methyl alcohol.

Add 1 ml of dilute sulphuric acid and 3 ml of potassium permanganate solution to 3-5 drops of alcohol, and in a few minutes add another 2 ml of sulphuric acid. The solution must be colourless. If the colour of $KMnO_4$ does not disappear, add a little of sulphite until the solution is decolourized. Add an equal volume of Schiff's reagent.

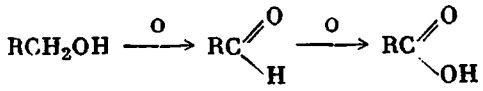
In 5-10 minutes, compare the colour of solutions containing methyl alcohol and free of it.

In an acid medium, dichromates are strong oxidants:

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

This reaction occurs if oxygen is consumed in oxidation of any substance. The change in the valence of chromium that occurs in this reaction accounts for the colour change from orange to green. The intermediate products in this reaction are probably acid esters of

chromic acid. Primary alcohols are oxidized in these conditions mainly to aldehydes, and the aldehydes are then slowly oxidized to the corresponding acids:



Further oxidation can be prevented by heating the volatile aldehyde and hence removing it from the reaction mixture.

In conditions of Experiment 45, methyl alcohol is quickly oxidized to formic acid and further to carbonic acid.

Oxidation of primary alcohols by potassium permanganate, which is decomposed according to the equation

$$2KMnO_4 + H_2O \longrightarrow 2MnO_2 + 2KOH + 3O$$

is more energetic compared with oxidation by dichromates (Experiments 45 and 46) and gives mainly salts of the corresponding organic acids. Being poorly dissociated in solution (see Experiment 75), these acids are displaced from their salts by mineral acids such as sulphuric or hydrochloric acid. The oxidation with permanganate is more energetic in a strongly alkaline medium.

Primary alcohols, including methyl alcohol, are oxidized with potassium permanganate, in an acid medium at room temperature, mainly to aldehydes. Secondary alcohols are converted to ketones by the action of oxidants. Tertiary alcohols are oxidized with difficulty and give a mixture of splitting products.

In conditions of Experiment 48, ethyl alcohol forms acetaldehyde, and methyl alcohol forms formaldehyde. Only formaldehyde reacts with Schiff's reagent in an acid medium to give the colour reaction characteristic of aldehydes (see Experiment 61).

49
Derivation of Iodoform from Alcohol

REAGENTS

Methyl alcohol.
Ethyl alcohol.
Their close homologues (see Table 3).
Ethylene glycol.

Carry out parallel experiments with ethyl and other alcohols.

Mix 3-4 drops of alcohol with 2-3 ml of water in a test tube, heat gently the solution (better on a water bath at 60 °C), and add

0.5-1 ml of iodine solution. Next add, drop by drop, dilute alkali solution until the colour vanishes. A pale yellow turbidity or precipitate and characteristic odour indicate the formation of iodoform.

In conditions of the experiment, iodine and alkali enter into a reversible reaction:

$$I_2 + 2NaOH \rightleftarrows H_2O + NaI + NaOI$$

The resultant salt of hypoiodous acid is a strong oxidant and it converts primary alcohols into aldehydes:

$$RCH_2OH + NaOI \longrightarrow RC\begin{matrix}/\!\!/ O \\ \backslash H\end{matrix} + NaI + H_2O$$

Secondary alcohols are oxidized to ketones.

Hydrogen atoms in the groups $-CO-CH_3$, $-CO-CH_2-$, and $-CO-CH\langle$ are readily replaced by halogens (see Experiments 36 and 37), by iodine in particular. If a compound containing $CI_3C\begin{matrix}/\!\!/ O \\ \backslash R\end{matrix}$ (where R is a hydrogen atom or a hydrocarbon radical) is formed by this reaction, it is easily decomposed in an alkaline medium to give iodoform and a salt of the corresponding acid:

$$CI_3-\overset{|}{\underset{|}{C}}\begin{matrix}/\!\!/ O \\ \backslash R\end{matrix} + H-\quad ONa \longrightarrow CHI_3 + RCOONa$$

In a similar way, chloroform and bromoform are formed, if chlorine and bromine are used to replace hydrogen.

The mechanism of the reaction was proved by experiments with deuterium (heavy hydrogen, ^2H or D). They showed that the hydrogen atom that passes to halogen-bonded carbon is eliminated from the alkali molecule.

It follows that iodoform can be obtained only from alcohols containing the metyl group at the primary or secondary (never tertiary) carbon atom bonded with the hydroxyl, i.e. from alcohols containing in their molecules the group CH_3CHOH, which is oxidized to give the group CH_3CO-. Hence, iodoform cannot be prepared from methyl, isoamyl, *n*-propyl or *n*-butyl alcohols in the conditions of this experiment, whereas ethyl or isopropyl alcohols can produce iodoform.

The negligibly small solubility of iodoform in water makes it possible to detect even traces of ethyl alcohol in an aqueous solution.

Aldehydes and ketones containing the group $CH_3—CO—$ readily give iodoform when acted on by iodine and alkali (see Experiment 73). The corresponding oxy- and keto acids, such as lactic acid, $CH_3CH(OH)COOH$, pyruvic acid, $CH_3COCOOH$, levulinic acid, $CH_3COCH_2CH_2COOH$, also give iodoform in similar conditions. Iodoform can also be obtained from some substances having quite different structures, e.g. citric acid, inositol. Acetic acid does not produce iodoform in these conditions.

50
Dehydration of Glycerol

REAGENTS

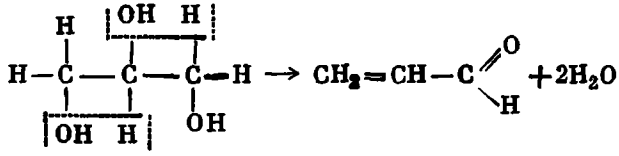
Glycerol.

Potassium bisulphate, or *sodium bisulphate*, powder. If bisulphate is not available it can be produced in the laboratory in the course of the experiment. To do so, mix 0.5-0.6 g of potassium sulphate with 5-6 drops of concentrated sulphuric acid in a dry test tube, and only then add glycerol.

USE THE HOOD.

Place a few drops of glycerol into a dry test tube, and add about 1 g of sodium (potassium) bisulphate. Shake the mixture, and heat carefully: disagreeable pungent odour indicates the formation of acrolein (see Experiment 66: preparing acrolein in solution).

As water is eliminated from the glycerol molecule, some substances are formed. One of them is an unsaturated aldehyde, acrolein



Small amounts of acrolein are formed by strongly heating glycerol (either free or bound in a molecule of fat), e.g. by burning fat on a hotplate. As glycerol is heated in the presence of bisulphates or free phosphoric acid, formation of acrolein is much facilitated. The process is likely to begin with the attack of the proton of the acid on the hydroxyl group at $C_{(2)}$ of the glycerol with elimination of water molecule and formation of a carbonium ion, $(HOCH_2)_2CH^+$, which then converts into acrolein with the loss of the proton and another molecule of water.

51
Complex-Formation of Polyhydric Alcohols

REAGENTS

Glycerol.
Mannitol.
Ethyl alcohol.
Ethylene glycol.
Borax, crystals.

A. Prepare copper hydroxide. To that end, add a small excess of caustic alkali to a dilute solution of copper sulphate.

Separate the greater part of the liquid on a small filter, and place small quantities of the precipitate into several test tubes using a glass rod or a spatula. Add 0.5-1 ml of water and 3-5 drops of liquid alcohol or about 0.1 g of solid alcohol (mannitol) into each test tube, omitting only one of them that should be kept as control. Shake the test tubes, allow their contents to settle and note development of specific colouration in some test tubes. Add dilute hydrochloric acid in excess to the solutions and observe the colour change.

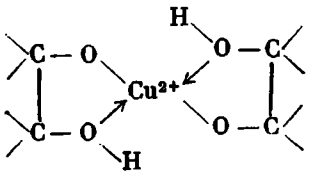
B. Shake about 0.5-1 g of crystalline borax and 10-15 ml of water in a test tube and allow the undissolved excess borax to settle down. Add 1-2 drops of phenolphthalein to the almost saturated borax solution.

Prepare test solutions in several test tubes as follows. Place 5-7 drops or 0.1-0.2 g of various alcohols and 2-3 ml of water into test tubes and shake. Add a drop of phenolphthalein and a drop of a dilute alkali solution into each test tube: the solutions turn bright crimson. Now add a small quantity of a coloured borax solution into each test tube.

As the two alkaline solutions are mixed together, the colour of some of them vanishes to indicate the acid reaction of the resultant mixture. Significant quantities of borax are required to make the solution react alkaline.

The ionization of hydrogen atoms in hydroxyl groups increases with the number of these groups in the alcohol molecule. Polyhydric alcohols are therefore slightly acid. In aqueous solutions, the ionization constant of a trihydric alcohol, glycerol, is close to 7×10^{-15}, and that of a hexahydric alcohol, mannitol, to 3×10^{-14} (see Experiment 75). For the purpose of comparison, it should be noted that the ionization constant of a quite weak acid, aqueous solution of hydrogen sulphide, is 5×10^{-8} for the first ionization, and 1×10^{-15} for the second ionization step. Monohydric alcohols are not appreciably ionized.

The acid properties of polyatomic alcohols cannot be detected by ordinary colour indicators, but they account for the great easiness with which the corresponding salt-like compounds, alcoholates, are formed by the action of alkali metals and many metal hydroxides, the reaction being similar to that of neutralization (see Experiment 124, and explanations to Experiment 40). If a molecule of an alcohol has two neighbouring hydroxyl groups, the alkaline solution of copper hydroxide first forms copper alcoholate that is converted into a complex cation with four hydroxyl groups (i.e. two alcohol molecules) having the coordination number 4. The complexing agent in this compound is cupric ion that replaces hydrogen in two —OH groups; the ligands are oxygen atoms of these two hydroxyl groups and also of two other groups that do not lose hydrogen atom.

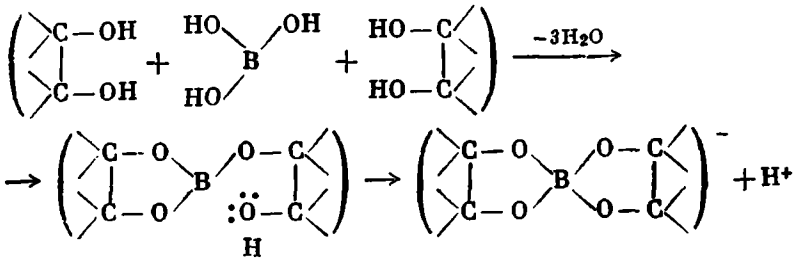


The complex ions account for the intense blue or violet colour of the solution (cf. Experiments 90, 119, and 125). The HO^- ion can be one of these ligands.

These compounds are stable to alkali, but acids destroy them to give the starting alcohol and the copper salt of the acid used in the experiment. The colour of the solution either vanishes or its intensity sharply decreases. Copper hydroxide quickly precipitates in water and in ethyl alcohol solution, and the supernatant liquid becomes clear.

Borax solution (crystalline sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$) is strongly alkaline because of the hydrolysis of a salt of a strong base and a very weak acid. The solution contains not only the $B_4O_7^{2-}$ ion, but also molecules of free boric acids (product of hydrolysis), including orthoboric acid, H_3BO_3, which can produce esters with alcohols (see Experiment 55). Three hydroxyl groups of two alcohol molecules take part in the reaction in Experiment B with polyhydric alcohols. Stabler cyclic esters are formed as a result. The neighbouring fourth hydroxyl group eliminates the hydrogen atom in the form of free hydrogen ion: the second ring is closed at the boron atom. Boron is thus a complexing agent having the coordination number 4, and its outer electron shell is filled to the octet by the electron pair of

the oxygen atom. These complexes are quite strong acids:



Such complexes with boric acid form also sugars in which at leas two neighbouring hydroxyl groups are in the *cis*-position.

Polyhydric alcohols have been studied in detail by S.N. Reformatsky.

52
Reaction of Ethyl Ether with Acids (Formation of Oxonium Compounds)

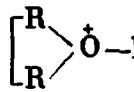
REAGENTS

Ethyl ether.

Place 2 ml of concentrated sulphuric acid into a test tube, and 2 ml of concentrated hydrochloric acid into another one. Cool the acids to 0 °C (in water mixed with snow or ice), and add carefully in small portions, with shaking and cooling, 1 ml of ethyl ether (also cooled) into each test tube. Note if the resultant homogeneous solutions smell of ether.

Measure out 5 ml of cold water containing pieces of ice into test tubes, and transfer each obtained solution into the water with shaking and cooling. The odour of ether can be sensed, and the ether layer rises to the surface. Add carefully a few drops of dilute alkali solution to neutralize part of the acid: the ether layer markedly increases.

Repeat the experiment, modifying the procedure as follows: the ether solutions in acids obtained as described above should first be heated to boiling, cooled, and only then transferred into water. Observe resinification of the mixture containing sulphuric acid.

Ethers react with concentrated acids to form complex oxonium compounds of the type  , where X^- is a halide ion or the acid radical. The reactions by which these compounds are formed are usually exothermic.

As the obtained solutions are diluted with water, the complexes fall into the starting components, the decomposition being accelerated with neutralization of the acid. Free ether forms a supernatant layer if the quantity of water is insufficient to dissolve it. Ethyl ether dissolves at room temperature about 1 per cent of water and water dissolves about 6 per cent of ether (by volume). Ethyl ether dissolves in diluted hydrochloric acid markedly better than in water or dilute sulphuric acid.

As ether is heated with sulphuric acid, ethylsulphuric acid is first formed:

$$(C_2H_5)_2O + 2H_2SO_4 \longrightarrow 2C_2H_5OSO_2OH + H_2O$$

which, on further heating, is partly decomposed with liberation of ethylene, and partly resinified and oxidized with excess sulphuric acid.

Of hydrohalic acids, only hydriodic acid relatively easily splits the ether molecule.

53
Formation of Complex Organic Compounds Containing Oxygen

REAGENTS

Ethyl ether.
Butyl alcohol, or *amyl alcohol.*
A mixture of petroleum hydrocarbons (see Chapter 4).
Chloroform.
Iodine, crystals.
Ammonium (*potassium*) *thiocyanate*, 1 per cent solution.

Carry out parallel experiments with several organic liquids containing and not containing oxygen in the molecule.

A. Place 0.5-1 ml of each substance into a dry test tube and add a small crystal (smaller than the size of a pin head) of iodine into each test tube. Shake the contents.

B. Mix approximately equivalent quantities of ferric chloride and ammonium (potassium) thiocyanate in a separate test tube to prepare 1-2 ml of a scarlet solution of ferric thiocyanate.

Add a drop of this solution and 2-3 ml of water to 0.5-1 ml samples of each test substance. Shake the mixtures strongly and allow to stand for layer separation.

Note the different colour of the solutions in the test tubes both in A and B.

Iodine vapour is violet. Iodine solutions in hydrocarbons (or their halogen derivatives) are coloured similarly. This indicates that

the dissolved iodine does not react with these solvents. But iodine reacts with organic substances containing oxygen in their molecule, and also with water, to produce unstable complex compounds of the oxonium type (see Experiment 52); the compounds are yellow, reddish or brown. If a test substance is solid, it should be dissolved in benzene or gasoline, and the colour of iodine solution in this mixture should be compared with that of iodine solution in pure solvent. For the same reason (complex-formation) the intensely coloured thiocyanate dissolves in organic compounds containing oxygen and in their solutions in benzene.

54
Preparing Ethyl Nitrite and Its Properties

REAGENTS

Ethyl alcohol.
Sodium nitrite, crystalline.

Dissolve 1 g of sodium nitrite in 2 ml of water (in a test tube) and add 1-1.5 ml of alcohol. Cool the test tube in a mixture of water and snow or ice. Mix 1 ml of concentrated hydrochloric acid with 1 ml of water in another test tube and also cool the mixture to 0 °C. Carefully pour the acid in small portions into the sodium nitrite solution with shaking and cooling the mixture. A yellowish layer of ethyl nitrite having a fruity odour floats to the surface above water.

A. Place a few drops of the obtained ester onto a watch glass and observe its volatilization.

B. Using a pipette, take a few drops of ethyl nitrite (avoiding water) and transfer the ester into another test tube containing 1 ml of water cooled to 0 °C. Add 1-2 drops of potassium iodide. Note the poor solubility of ethyl nitrite in water and the absence of iodine liberation. Add 1-2 drops of hydrochloric acid and shake. Observe the changes.

C. Mix a few drops of ethyl nitrite with 1 ml of cold water, add 1-2 drops of alkali solution and shake the mixture: the ester layer disappears, and the fruity odour is no longer smelt.

Esters of nitrous acid, alkyl nitrites, are noted for the easiness and rapidity with which they are formed from the corresponding alcohol and nitrous acid as the latter is liberated in the free state:

$$NaNO_2 \xrightarrow{HCl} HNO_2 \xrightarrow{ROH} RON{=}O$$

Nitrous acid is unstable and its esters formed from simple alcohols are highly volatile. The reaction mixture should therefore be effectively cooled.

Alkyl nitrites are markedly less soluble in water than the starting alcohols, since the hydroxyl group is absent from the ester molecule.

Alkyl nitrites are hydrolysed in neutral aqueous solutions rather slowly. The process is significantly accelerated in the presence of alkali or free mineral acid (see Experiments 93-95). The hydrolytic action of acids is easily detected by the formation of free nitrous acid, HNO_2, which is unstable and decomposes with liberation of nitrogen oxides. The acid liberates iodine from iodides in an acid medium:

$$2H^+ + 2I^- + 2HNO_2 \longrightarrow I_2 + 2H_2O + 2NO$$

Inhalation of ethyl nitrite vapour can cause tachycardia and reddening of the face.

55
Formation of Boric Acid Ester

REAGENTS

Methyl alcohol or *ethyl alcohol.*

Boric acid, crystalline.

Heat 1.5-2 g of boric acid in a test tube holding it horizontally. From time to time heat the test tube walls over the flame to remove droplets of water. The acid gradually loses its water and melts. As the last crystals of the acid disappear, allow the test tube to cool in the horizontal position: the thick clear melt hardens and partly cracks. Add 4-5 ml of alcohol, 2 ml of concentrated sulphuric acid, and a boiling stone. Close the test tube with a stopper through which a gas outlet tube is passed, and connect the tube to a condenser. Distil 1-2 ml of liquid into a dry test tube.

Transfer part of the distillate onto a watch glass and light up: note the characteristic colour of the flame and liberation of incombustible products that produce a white deposit on a cold glass. Add water, drop by drop, to the remaining part of the distillate.

As boric acid, H_3BO_3, is heated, it is gradually dehydrated to form metaboric acid, HBO_2, tetraboric acid, $H_2B_4O_7$, and finally boric anhydride, B_2O_3. The anhydride is the main bulk of the vitreous melt. In an acid medium, alcohols quickly react with boric anhydride

to give volatile esters:

$$B_2O_3 + 6ROH = 2B(OR)_3 + 3H_2O$$

that are distilled together with excess alcohol.

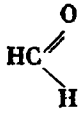
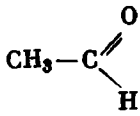
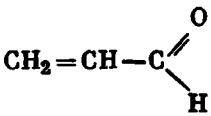
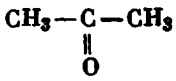
Trimethyl borate burns with a white smoke that produces a white coat on cold objects (boric acid). The flame is beautifully tinged bright green. If water is added to the ester, it quickly hydrolyses with precipitation of boric acid crystals that dissolve in excess water. Triethyl borate is formed somewhat slower. The ester is less volatile, its flame green only on the margins, and the hydrolysis in water in the cold is slower. Boric acid esters react with excess alcohol to give complex compounds characterized by acid properties (cf. Experiments 51 and 52).

ALDEHYDES AND KETONES

Chemical properties of aldehydes of the fatty series are vividly illustrated by formaldehyde, acetaldehyde, and acrolein. Acetone is the most available ketone of the fatty series. All these substances can easily be prepared in the laboratory during the experiments (see Experiments 56, 57, 58, and 67). But in Experiments 64 and 68-72 relatively large quantities of the starting substances are required, and commercial formalin and acetone should therefore be kept in the laboratory. Physical properties of some aldehydes and ketones are given in Table 4.

Table 4

Properties of Aldehydes and Ketones

Substance	Formula	M. p., °C	B. p., °C	Density, g/cc
Formaldehyde		−92	−20	—
Acetaldehyde		−124	21	0.78
Acrolein		−88	52	0.84
Acetone		−95	56	0.79

Commercial formaldehyde is a 30-40 per cent aqueous solution commonly known as formalin (density 1.09 g/cc). Whenever necessary, formalin can be diluted with water.

Commercial formalin usually contains methyl alcohol and formic acid admixtures, and reacts slightly acid. On long storage formalin forms a white precipitate, polymer paraformaldehyde $(HCHO)_n$, and the formaldehyde content of the solution thus sharply decreases. To increase formaldehyde concentration, about 0.5-1 per cent (by volume) of a 20-25 per cent alkali solution is added to the formalin containing paraform, the mixture is stirred and heated to 60-70 °C on a water bath. The paraform precipitate is completely dissolved in a short time. If new portions of paraformaldehyde are added, the concentration of formaldehyde can be raised to 40 per cent and over. Before the experiment, the alkali-treated formalin should be neutralized against phenolphthalein with 5-10 per cent hydrochloric or sulphuric acid. An alkaline solution (without neutralization) can be used in Experiment 59. The paraformaldehyde precipitate can also be dissolved (depolymerized) by boiling formalin with 0.5-1 per cent (by volume) of concentrated sulphuric acid. The acid formalin can be used in Experiments offered in this Chapter, but it should be neutralized for use in Experiments of Chapter 20 (condensation). Depolymerization with alkali should be preferred.

Simpler aldehydes and ketones are miscible with water in any proportion. The solubility of aldehydes and ketones usually decreases with the growing number of carbon atoms in the radicals.

56
Formation of Acetaldehyde by Oxidation of Ethyl Alcohol

REAGENTS

Ethyl alcohol.
Potassium dichromate, powder.

Place 0.5 g of potassium dichromate in a test tube and add 2 ml of dilute sulphuric acid and 2 ml of alcohol. Shake the mixture. The solution becomes hot and its colour changes.

Fix the test tube in the stand in an inclined position, attach a gas outlet tube, and lower its other end in another test tube (receptacle) containing 2 ml of cold water. Place the receptacle in a beaker containing cold water. Carefully heat the reaction mixture over the flame of a burner avoiding bumping of the boiling mixture. The liquid volume in the receptacle is almost doubled in 2-3 minutes of boiling. Stop heating and dismantle the apparatus.

The distillate in the receptacle has the pungent odour of acetaldehyde. Use the solution in Experiments 59-61 and 63.

The reaction of alcohol oxidation with potassium dichromate was discussed above (Experiments 45-48).

The obtained aqueous solution, in addition to the main distilled product, acetaldehyde, also contains alcohol, acetic acid, and acetal. The latter product is formed by the action of acetaldehyde on non-oxidized alcohol:

$$CH_3C\begin{matrix}\diagup\!\!\!\!\diagup O \\ \diagdown H\end{matrix} + 2HOC_2H_5 \longrightarrow CH_3CH(OC_2H_5)_2 + H_2O$$

As alcohol is oxidized, small quantities of other side products are formed, e.g. ethylsulphuric acid, ethyl acetate, paraldehyde, carbon dioxide, sulphur dioxide (see Chapter 6).

57
Formation of Aldehydes from Alcohols by Elimination of Hydrogen (Dehydrogenation)

REAGENTS

Methyl alcohol.
Ethyl alcohol.
Copper metal (fine wire gauze).

Carry out parallel experiments with ethyl and methyl alcohols.

Select a cork stopper for a common test tube. Bend a strip of fine copper gauze into a dense cylinder that freely enters the test tube to fill its almost entire volume. The length of the copper cylinder should be 4-5 cm.

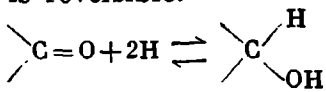
Place 3 ml of the test alcohol and 2 ml of water in a dry test tube. Strongly heat the copper gauze in the flame of a burner, holding the gauze by crucible tongs: copper soon blackens. Quickly insert the gauze into the test tube containing the alcohol and close it immediately (not tightly!) with the stopper. Alcohol vigorously boils, and the odour of aldehyde can be smelt. The copper gauze becomes bright red.

When alcohol ebullition stops, fit the cork stopper tightly in the test tube and cool it in a beaker containing cold water. Remove the stopper, transfer the liquid into another test tube, and add an approximately equal volume of water, which was first used to rinse the copper gauze in the former test tube.

The water-alcohol solution of formaldehyde thus obtained (from methyl alcohol) or acetaldehyde (from ethyl alcohol) gives all

reactions characteristic of aldehydes (see Experiments 59-61). This solution is recommended for further experiments; make sure (in parallel tests) that the starting alcohol does not give these reactions.

The reaction of reduction of the carbonyl group of aldehydes and ketones with hydrogen (with formation of the corresponding alcohols) is reversible:



As hydrogen and aldehyde, which is more volatile than alcohol, are quickly removed from the reaction zone, the equilibrium is shifted to the left, i.e. in the direction of alcohol dehydrogenation. Many metals accelerate catalytically the direct and the reverse reaction. The equilibrium is quickly attained in the presence of copper at 300-350 °C, and in the presence of finely crushed platinum, at room temperature. In addition to aldehyde and hydrogen, the dehydrogenation of alcohols also gives small quantities of side products, such as the corresponding acids, and also carbon monoxide and carbon dioxide.

As a copper gauze is ignited in air, its surface is partly oxidized. The fine coat of copper oxide thus formed is readily reduced in the hot state with alcohol and turns from black to bright red.

In industry, aldehydes are manufactured by dehydrogenation of alcohols.

58
Formation of Acetaldehyde by Hydration of Acetylene (Kucherov's Reaction)

REAGENTS

Calcium carbide.
Mercuric oxide, yellow.

Prepare acetylene in a test tube or a small flask as instructed in Experiment 25. Place 3-5 g of calcium carbide into a test tube (flask), close it tightly with a stopper provided with a dropping funnel, the end of which is drawn. A common funnel can be used as well, but its stem should be connected to a glass tube with a drawn end through a rubber tubing with a clamp.

Pass the acetylene thus formed into another test tube closed with a stopper through which two tubes are passed: one for delivery of acetylene (with a drawn end, reaching almost to the bottom) and the other tube for gas outlet. The latter tube is connected with an-

other tube that delivers the volatile reaction products and excess gas to a receptacle containing 1-3 g of snow or ice and cooled on the outside with water and snow.

Place 0.2 g of mercuric oxide, 4 ml of water, and 2 ml of concentrated sulphuric acid in a reactor. As the hot mixture is shaken, the greater part of mercuric oxide dissolves. Now stopper the reactor tightly with a plug through which the acetylene tube is passed. Place the reactor into a beaker filled with water heated almost to boiling. Slowly add water from the funnel into the carbide vessel and adjust the acetylene flow so that the liquid does not overflow from the reactor into the receptacle, and the gas passes at a rate of a bubble per second (or two seconds).

Very soon white flakes precipitate in the reactor. Discontinue acetylene passage in 10-15 minutes and dismantle the apparatus. The liquid in the receptacle strongly smells of acetaldehyde and gives all qualitative reactions for acetaldehyde (see Experiments 59-61 and 63).

Hydration of acetylene and its homologues at the triple bond in the presence of mercuric salts was opened by M.G. Kucherov and discussed in detail in many of his papers (1875-1909). The mechanism of the reaction is as this:

$$-C\equiv C- \xrightarrow{+H_2O} -\underset{\underset{O}{\|}}{C}-CH_2-$$

Acetylene itself produces acetaldehyde with liberation of much heat. The reaction proceeds in a strongly acid medium. In the conditions of the experiment, mercuric sulphate is formed, which is attached at the triple bond of acetylene. The sparingly soluble product thus formed reacts with water at a temperature of the order of 100 °C to give acetaldehyde, whereas mercuric sulphate is recovered to bind the acetylene molecule again. The process is thus repeated. The intermediate product is probably vinyl alcohol, which is then isomerized into aldehyde. In addition to acetaldehyde, small quantities of side products, such as acetone, diacetyl, crotonaldehyde, and acetic acid, are formed.

The Kucherov reaction is widely used in industry for the manufacture of acetaldehyde, which is then converted into acetic acid, ethyl alcohol, and synthetic rubber.

In conformity with the Markownikoff rule, acetylene homologues form ketones in the conditions of the Kucherov reaction.

The Kucherov reaction is characteristic of hydrocarbons containing triple bonds. Double-bond hydrocarbons also give compounds with mercuric salts, but they are not hydrated in the described conditions.

59
Reduction of Cupric Compounds with Aldehydes

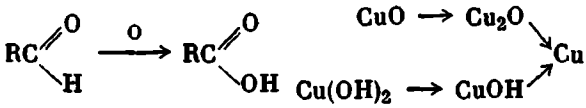
REAGENTS

Formaldehyde solution (see Experiment 57).
Acetaldehyde solution (see Experiments 56-58).

Add 0.5 ml of dilute alkali solution to 1 ml of an aldehyde, and then add, drop by drop, copper sulphate solution until a precipitate falls out. Heat the obtained mixture to boiling: the colour of the precipitate changes.

Copper sulphate reacts with alkali to form a blue precipitate of cupric hydroxide, $Cu(OH)_2$. As the hydroxide is heated, it loses its water and gives black copper oxide, CuO.

Aldehydes are readily oxidized to the corresponding carboxylic acids, i.e. they are strong reductants. When heated in an alkaline medium they reduce cupric compounds to cuprous compounds, and further to copper metal:



All compounds given above are sparingly soluble in alkali solutions and precipitate with specific colouration: cuprous hydroxide, CuOH, is yellow and cuprous oxide, Cu_2O, is red. Copper metal is recovered as a brownish red powder. The course of the reaction can thus be easily followed up by the colour change of the precipitate. The reaction was proposed by Trommer.

Oxidation of aldehydes is accelerated in the presence of excess free alkali. Aromatic aldehydes do not give this reaction (see explanations to Experiment 181).

In conditions of this experiment, acetaldehyde reduces copper(II) oxide mainly to copper(I) oxide. Formaldehyde is not only oxidized, but in the presence of catalysts (Cu_2O or Ag_2O) it reacts with alkali:

$$HCHO + NaOH = HCOONa + H_2$$

The liberated hydrogen reduces copper or silver compounds to the corresponding pure metal (see next experiment).

60
Reduction of Silver Compounds with Aldehydes

REAGENTS

Formaldehyde solution (see Experiment 57).
Acetaldehyde solution (see Experiments 56, 57, 58).

First prepare an ammoniacal solution of silver oxide. Act as follows. Place 4-5 ml of silver nitrate solution in a test tube and add a dilute aqueous solution of ammonia, drop by drop, until the precipitate that first falls out is all dissolved.

Place 1 ml of aldehyde solution into two test tubes and add 1 ml of the fresh ammoniacal silver oxide into each test tube. Add 2-3 drops of dilute alkali solution into one test tube. Shake the tubes and place them in the stand.

Note in which of the two test tubes the change appears sooner. If silver is not precipitated, heat the test tubes for a few minutes on a water bath at 50-60 °C.

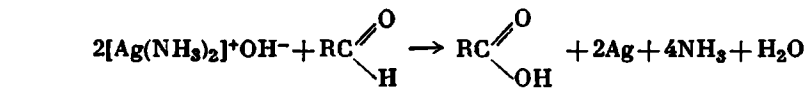
To deposit a silver mirror on the test tube walls, wash the test tube thoroughly before the experiment with a hot alkali solution and rinse with distilled water.

At the end of the experiment wash the glassware that contained the ammoniacal silver oxide, and dissolve the precipitates and coats on the walls with dilute nitric acid.

An insoluble silver oxide, Ag_2O, which is formed in an alkaline medium from the silver salts, is dissolved in the presence of excess ammonia to form an ammonia complex:

$$Ag_2O + 4NH_3 + H_2O \longrightarrow 2[Ag(NH_3)_2]^+OH^-$$

Aldehydes are readily oxidized to reduce silver compounds in an alkaline medium to silver metal. This is the qualitative reaction for aldehydes that was suggested by Tollens in 1881. In our experiment the reaction equation is as follows:



(see also the previous experiment).

Excess hydroxyl ion, which is attained by adding caustic alkali, accelerates oxidation of aldehydes in our case. Considerable excess of ammonia decreases the sensitivity of the reaction.

A black precipitate of silver nitride, Ag_3N, sometimes falls out from ammoniacal silver oxide on long standing. When disturbed, the precipitate explodes even in the moist state. The ammoniacal

solution of silver oxide should therefore be prepared immediately before the experiment and in the quantity not exceeding the need of the experiment.

Aldehydes differ from ketones in that they reduce salts of copper and silver in alkaline solution. Ketones are not usually oxidized so easily. But other strong organic reductants, such as many polyhydric phenols, aromatic amines, aminophenols, hydroxyketones, react with salts of silver and copper as rapidly as aldehydes.

In an alkaline medium, acetone does not react with copper salts but reduces salts of silver.

61
Reaction of Aldehydes with Schiff's Reagent

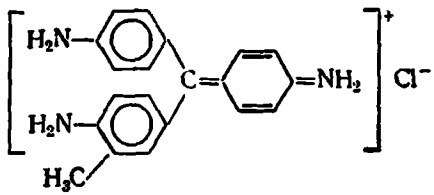
REAGENTS

Formaldehyde solution (see Experiment 57).
Acetaldehyde solution (see Experiments 56-58).
Schiff's reagent solution.

To prepare Schiff's reagent, dissolve 0.2 g of fuchsin in 200 ml of distilled water and add a few millilitres of almost saturated solution of sulphur dioxide in water (or 2 g of sodium bisulphite and 2 ml of concentrated hydrochloric acid). If the liquid is not decolourized in 15-20 minutes, add a little activated carbon, shake, and separate the clear solution by filtration. Keep the reagent in a well stoppered vessel in the dark. The sensitivity of the reagent decreases with growing excess of sulphur dioxide.

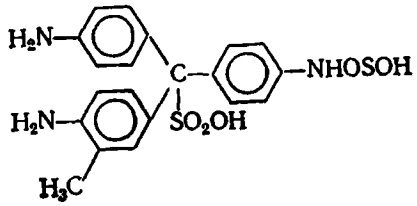
Place 1-ml portions of colourless Schiff's reagent into two test tubes and add a few drops of formaldehyde into one of them and the same quantity of acetaldehyde into the other test tube. Note the colour of the solutions in the test tubes. Now add 0.5 ml of concentrated hydrochloric (or dilute sulphuric) acid and note the colour changes again, immediately after adding the acid, and in 5-10 minutes.

Fuchsin (rosaniline) is a derivative of triphenylmethane:

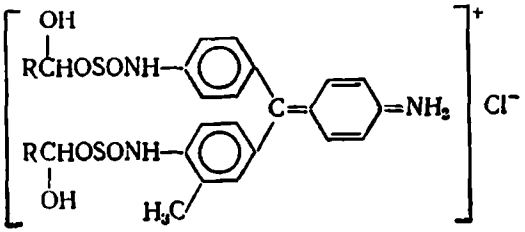


Its red colour is due to the quinonoid structure (see explanations to Experiment 234). As two molecules of sulphurous acid are joined

to fuchsin, a colourless compound is formed. The quinoid grouping is absent from Schiff's reagent:



As aldehydes combine with Schiff's reagent, the structure is altered and new substances are formed whose structure is quinonoid. Their colour is therefore the same as that of fuchsin, except that the hue is deeper blue:



These compounds react gradually with excess sulphurous anhydride to eliminate aldehyde as its bisulphite compound (see Experiment 70) and convert back to free Schiff's reagent. The solution is therefore decolourized on standing.

As mineral acids are added in a great excess, both the starting fuchsin (see Experiment 234) and the coloured products of aldehyde addition to Schiff's reagent are decolourized, except the corresponding derivative of formaldehyde, which is stabler and retains its colour in the presence of strong acids. True, its hue becomes deeper blue. Thus the colour reaction with Schiff's reagent in a strongly acid medium can be used to differentiate formaldehyde from other aldehydes (cf. Experiment 48).

On long storage, by the action of heat or alkalis and salts having alkaline reaction (due to hydrolysis in water), and also by the action of cupric salts, amines, and substances that bind SO_2, the colourless solution of Schiff's reagent can be coloured through elimination of sulphurous acid and appearance of free fuchsin.

The test with Schiff's reagent is very sensitive and specific for aldehydes. Ketones do not generally give this reaction, but some of them bind sulphurous acid to colour the solution pink.

The reagent was proposed for detection of aldehydes by Hugo J. Schiff in 1866.

62
Polymerization of Formaldehyde

REAGENTS

Formalin, commercial.

A. Weigh a watch glass, place 3 ml of formalin on it, and evaporate to dryness on a boiling water bath in the HOOD. Wipe the watch glass on the outside, cool, and weigh again.

B. Place 3 ml of formalin in a test tube; cool the test tube in water and shake, and add 1 ml of concentrated sulphuric acid: a white precipitate falls out. In 20-30 minutes, add 5 ml of water, suck the product on a funnel with a disc (see Experiment 1), wash with a few drops of water, dehydrate, dry in paper, and weigh.

C. Compare the solubility of the polymers obtained in A and B (separately) in water at room temperature and with heating.

D. Place the samples of both polymers in test tubes and keep in the flame of a burner. Observe the sublimation of the polymer onto the test tube walls. Smell carefully the odour of the sublimed polymers.

Almost the entire formaldehyde is present in its aqueous solution in the form of the hydrate, $CH_2(OH)_2$. It is therefore impossible to obtain anhydrous formaldehyde by distillation, although its boiling point is very low (—21 °C). As water is gradually evaporated from formalin, part of formaldehyde is volatilized together with water, whereas the main bulk is polymerized with the loss of water to form long chains

$$n CH_2O \longrightarrow (CH_2O)n$$

The end units of the chain contain free OH groups. Solid polymer, paraformaldehyde, obtained in these conditions, is well soluble in water, particularly with heating. On dissolution it forms formalin.

Dehydration of the formaldehyde hydrate by the action of concentrated sulphuric acid gives a higher polymer (over 100 molecules in a chain) that is insoluble in water.

Formaldehyde polymers with even longer chains have recently been obtained. They are used as valuable plastic materials.

On strongly heating, formaldehyde polymers are depolymerized to give a gaseous monomer with a pungent odour, which immediately polymerizes (almost fully) on the cold walls of the test tube in the form of a predominantly cyclic trimer, trioxymethylene, $(CH_2O)_3$. Its melting point is 62 °C.

63
Condensation of Acetaldehyde in Alkaline Medium

REAGENTS

Acetaldehyde solution (see Experiments 56 or 58).

Place 1-2 ml of acetaldehyde solution in a test tube and add half volume of a dilute alkali solution. Heat the mixture slowly until it starts boiling. Soon the odour of the liquid becomes pungent, the liquid turns yellow, then brown, and an oily liquid, "aldehyde resin", is collected on the bottom of the test tube.

The carbonyl group $\rangle C{=}O$ has the σ- and π-bonds and is strongly polarized with increasing electron density at the oxygen atom and decreasing density at the carbon atom. Hydrogen atoms at the neighbouring (second) carbon atom are protonized to become more accessible for the nucleophilic reagents (cf. explanations to Experiment 26). During condensation of aldehyde in an alkaline medium, the nucleophile, HO^- ion, detaches the proton from the second carbon atom. The formed carbanion $—CH_2CHO$ is also a nucleophile. It attacks the carbonyl carbon of the second molecule of aldehyde to form first the ion $CH_3CH(O^-)CH_2CHO$ that reacts with water to give a hydroxyaldehyde, aldol, $CH_3CH(OH)CH_2CHO$, with recovery of the ion HO^-. Aldol is unstable and eliminates water to give crotonaldehyde, $CH_3CH{=}CHCHO$, characterized by a pungent, suffocating odour.

Given sufficiently high concentration of the alkali, aldehyde condensation can proceed further to give high-molecular coloured resinous products. Condensation of other, more complicate, aldehydes of the fatty series proceeds in a similar way. The process is known as the aldol condensation, since the first condensation product is ald l.

Formaldehyde does not give aldehyde resin in these conditions. Instead of glycolic aldehyde, $CH_2(OH)CHO$, which might be expected to be the product of the aldol condensation of formaldehyde, methyl alcohol and a formiate are formed:

$$2CH_2O + NaOH \longrightarrow CH_3OH + HCOONa$$

Acetaldehyde can also react similarly under certain conditions (Cannizzaro-Tishchenko reaction; see Experiment 180).

Under the action of milder condensing agents, e.g. calcium hydroxide, formaldehyde undergoes the aldol condensation to give (in addition to small quantities of glycolic aldehyde) mainly the pro-

ducts of condensation of six formaldehyde molecules that have all properties of sugars (A.M. Butlerov, 1859).

Ketones can also undergo condensation reactions, but in the described conditions they do not form resinous products characteristic of aldehydes. Halogen-substituted ketones and hydrooxyketones are readily resinified by alkalies.

64
Preparing Hexamethylenetetramine

REAGENTS

Formalin, commercial.

Place 5-7 ml of formalin in a calibrated porcelain dish and weigh to an accuracy of 0.1 g. Stir the liquid and add concentrated solution of ammonia until a distinct odour of ammonia is felt. Place the dish containing the slightly warm mixture on a gauze over a burner and evaporate (with stirring by a rod) to a small volume, and finally to dryness, on a boiling water bath. Weigh the dish containing the dry residue.

The yield of the dry crystalline substance, hexamethylenetetramine, is very close to theoretical, calculating with reference to formaldehyde content of the starting formalin.

Hexamethylenetetramine can be used in further experiments without purification. Whenever necessary, it can be recrystallized from 80-90 per cent alcohol solution.

65
Reactions of Hexamethylenetetramine

REAGENTS

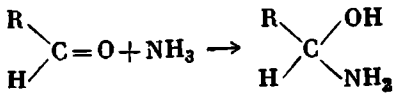
Hexamethylenetetramine (see Experiment 64).

A. Add 1 ml of dilute sulphuric acid to 0.2-0.5 g of hexamethylenetetramine and heat the mixture to boiling: specific odour of formaldehyde can be smelt. Cool the liquid slightly, add carefully 1 ml of concentrated alkali solution, heat again to boiling, and smell carefully the odour of the evolving vapour.

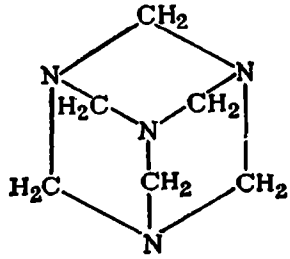
B. Dissolve 0.2-0.5 g of hexamethylenetetramine in 2-3 ml of water and divide the solution into two parts. Add a few drops of silver nitrate solution to one part, and then pour the remaining hexamethylenetetramine into the mixture. Observe the changes.

C. Heat a few crystals of hexamethylenetetramine in a dry test tube and establish whether or not gaseous products having characteristic pungent odour are formed on its decomposition.

Aldehydes are attached to ammonia across the double bond of the carbonyl group



The products of addition are usually unstable and undergo further transformations. In the case with formaldehyde, hexamethylenetetramine (hexamine), $C_6H_{12}N_4$, is formed. Hexamethylenetetramine was first prepared by A.M. Butlerov in 1859. Its peculiar structure was established later. The molecule of hexamethylenetetramine has a complicate spatial structure, and its projection onto a plane has the following configuration:



As ammonia acts on formaldehyde polymers, hexamethylenetetramine is also produced. Formaldehyde homologues react with ammonia to give tetramines similar to hexamethylenetetramine and nitrogenous products of other types. The process of preparing hexamethylenetetramine is accompanied by parallel, more complex, processes, but the quantities of side products are insignificant.

The reaction of formation of hexamethylenetetramine is reversible:

$$6CH_2O + 4NH_3 \rightleftharpoons C_6H_{12}N_4 + 6H_2O$$

but the equilibrium is strongly displaced to the right. As hexamethylenetetramine is heated with acids, ammonia is bound, whereas volatile formaldehyde is removed from the reaction zone. Ammonia is removed on heating with alkali. In both cases the equilibrium shifts to the left, i.e. hexamethylenetetramine is hydrolysed.

Being a tertiary amine, hexamethylenetetramine forms many products of addition of halogens, acids, and salts. A nitrogen atom of the hexamethylenetetramine molecule is a complexing agent in these complex compounds. Hexamethylenetetramine does not reduce silver compounds to metal even with boiling, but it produces a white

precipitate of a complex compound, $C_6H_{12}N_4 \cdot AgNO_3$, with silver nitrate; the complex compound is soluble in excess hexamethylenetetramine because a complex compound having a different composition is formed. When heated carefully, dry hexamethylenetetramine is sublimed almost without decomposition; only a little ammonia is eliminated.

Pressed into tablets, hexamethylenetetramine is used as solid fuel for household purposes.

A molecule of hexamethylenetetramine has four six-membered rings. Substances having similar structures, but containing oxygen and carbon atoms instead of nitrogen atoms, have been obtained. Like hexamethylenetetramine they are volatile (despite the high molecular mass) and stable to heat.

66
Formation of Acrolein and Its Reactions

REAGENTS

Glycerol.
Potassium (sodium) bisulphate, powder.
Schiff's reagent (see Experiment 61).

USE THE HOOD.

Dehydrate glycerol as instructed in Experiment 50, but carry out the reaction in a test tube with a gas outlet tube whose end almost reaches the bottom of another test tube (receptacle) containing 1-2 ml of cold water, placed in a beaker filled with water. Heat the mixture of glycerol and potassium (sodium) bisulphate for 2-3 minutes until white fumes stop evolving. Disassemble the apparatus, leaving the reaction test tube in the hood. Add alkaline potassium permanganate to destroy residual acrolein.

The distillate has the pungent odour of acrolein. Divide the distillate into several portions and carry out reactions characteristic of aldehydes (Experiments 59-61) and unsaturated compounds (Experiments 18 and 19).

Formation of acrolein from glycerol has already been discussed (Experiment 50). In accordance with its structure, acrolein readily reacts with bromine, is oxidized with potassium permanganate in alkaline solution, and gives clear reactions for aldehydes.

67
Formation of Acetone

REAGENTS

Calcium acetate, anhydrous powder.

To obtain anhydrous calcium acetate, the dihydrate $(CH_3COO)_2Ca \cdot 2H_2O$ should be heated to 120-130° C and crushed.

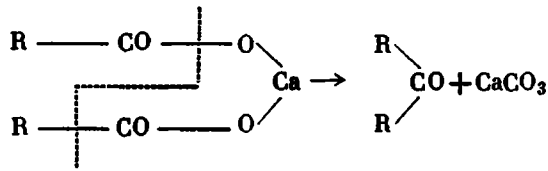
Place 4-5 g of dry calcium acetate into a test tube, connect a gas outlet tube, and fix the test tube in the stand almost horizontally, so that its bottom is slightly above its mouth. Tap slightly on the test tube to form a channel over the salt bed. Lower the gas outlet tube end almost to the bottom of a receptacle containing 2 ml of cold water and placed in a beaker filled with water.

Heat the test tube over a flame of the burner, first carefully and then stronger, and finally to redness. The salt partly chars and blackens. The volatile products of decomposition pass into the receptacle and the volume of the liquid in it approximately doubles in 5-7 minutes. Stop heating and dismantle the apparatus immediately.

The yellow distillate has a pungent odour and gives the iodoform reaction characteristic of acetone (see Experiments 49 and 73). If the distillate is cloudy (resinous particles), pass it through a small pleated filter wetted with water.

Allow the reaction test tube to cool down, add 2-3 ml of dilute hydrochloric acid to its contents and observe intense liberation of carbon dioxide. If the starting calcium acetate is acidified, carbon dioxide is not liberated.

Salts of carboxylic acids decompose at high temperatures with formation of ketones. The reaction with calcium salts is substantially as this:



Non-symmetrical ketones, i.e. those having different hydrocarbon radicals at the carbonyl group, are formed by heating a mixture of salts of two different acids. If calcium formate is added to the starting mixture, aldehydes are formed as well. Salts of dibasic acids give cyclic ketones in these conditions. Better yields of ketones are obtained with salts of barium and of some other metals, especially thorium (compared with calcium salts).

Pyrolysis of salts of carboxylic acids gives various side products, mainly gases, CH_4, CO, CO_2, C_2H_4, H_2, C_2H_2, etc. Acetone obtained

by this method is contaminated with the products of its decomposition at high temperatures. Carbon is one of them. Acetone is readily salted out from its aqueous solution by potassium carbonate (see Experiment 38). Unlike lower aldehydes, acetone is not hydrated in aqueous solutions (see explanations to Experiment 62).

68
Preparing Acetone Oxime

REAGENTS

Acetone, pure.
Hydroxylamine hydrochloride.
Sodium carbonate, anhydrous powder.

Place 7 ml of water into a wide test tube and dissolve 2 g of hydroxylamine hydrochloride and 1.5 g of anhydrous soda in it: much carbon dioxide is liberated. Cool the obtained solution well (better in ice-cold water) and add, with shaking, 1.5 ml of acetone: the mixture becomes hot and carbon dioxide is again liberated in ample quantities. Acetone oxime precipitates in the form of light white crystals. The odour is faint but specific. Cool the mixture for a few minutes, separate the crystals on a small funnel with suction, wash with 2-3 drops of cold alcohol and dry in filter paper. The yield is about 1 g.

Hydroxylamine hydrochloride reacts with soda to give free hydroxylamine, NH_2OH, melting at 33 °C, and readily soluble in water:

$$2NH_2OH \cdot HCl + Na_2CO_3 \longrightarrow 2NH_2OH + 2NaCl + CO_2 + H_2O$$

Part of carbon dioxide is liberated and part remains in solution in the form of unstable and readily hydrolysing carbonates of hydroxylamine.

Aldehydes and ketones react with hydroxylamine to give the oxime and water. The reaction with acetone is as follows:

$$(CH_3)_2C{=}O + H_2NOH \longrightarrow (CH_3)_2C{=}NOH + H_2O$$

Carbon dioxide is liberated again (binding of hydroxylamine).

Oximes are also formed by the reaction of aldehydes or ketones directly with a hydroxylamine salt solution, without its preliminary alkalizing. The indication of binding of hydroxylamine is the clearly acid reaction of the solution, but isolation of oxime crystals is difficult in these conditions.

In the formation of oximes, the nucleophile $:NH_2OH$, having an unshared electron pair, is first quickly added to the carbon of the carbonyl group (see explanations to Experiment 63) and the reac-

tion product, $(CH_3)_2C(OH)NHOH$, then loses (much slower) water to convert into oxime.

Acetone oxime melts at 60 °C; it is readily soluble in water, alcohol, ether; as the reaction mixture is strongly cooled, the solubility of the oxime decreases and its yield increases.

Many oximes readily crystallize and melt within a narrow range of temperatures. Preparing oximes is often used for identification of aldehydes and ketones.

69
Bromination of Acetone

REAGENTS

Acetone, pure.

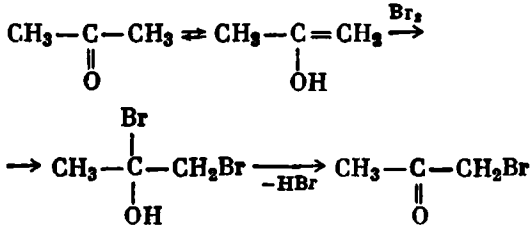
USE THE HOOD.

Place 0.5 ml of bromine solution in carbon tetrachloride in a dry test tube, and add a drop of acetone. Heat carefully the liquid coloured brightly with bromine: the solution is suddenly decolourized and hydrogen bromide liberated. Hydrogen bromide can easily be detected by a common test (Experiment 18).

Wet a strip of filter paper in the obtained colourless liquid and allow the solvent to evaporate almost completely. The odour of the bromoacetone thus formed is irritating (a powerful lacrimator).

Destroy bromoacetone residues with alkali solution (in the vessels used for the preparation of bromoacetone).

Like many aldehydes and ketones, acetone enters into some reactions in its tautomeric (enolic) form. For example, bromine is added across the double bond of enol; bromoacetone is formed by elimination of hydrogen bromide from the addition product:



The formed monobromoacetone, $CH_3—CO—CH_2Br$, (b.p. 138 °C) is evaporated on a filter paper slower than the solvent, carbon tetrachloride (b.p. 77 °C). The lacrimating action of bromoacetone can

be sensed in concentrations as low as 0.0015 mg in a litre of air.

Acetone reacts with chlorine in a similar way.

The quantity of enolic molecules of acetone at room temperature is only 2-3 per million, and the rate of enolization determines the rate of acetone bromination.

Halogenation of ketones is catalysed by acids and alkalis (see Experiment 73).

In reaction with more complicate ketones, halogens first replace the hydrogen atom at the atom of carbon bonded with the carbonyl group. If the halogen is taken in excess, the second and third atoms of hydrogen at the same carbon atom, if any, are also replaced by the halogen. Halogen-substituted ketones are usually lacrimators. Halogen atoms are not strongly bonded and can therefore be easily eliminated by alkali.

70
Reaction of Acetone with Sodium Bisulphite

REAGENTS

Acetone, pure.
Sodium bisulphite, saturated solution.

To prepare sodium bisulphite solution, mix dry sodium bicarbonate, or crushed sodium carbonate, $Na_2CO_3 \cdot 10H_2O$, with water taken in the quantity only to cover the crystals with a thin liquid layer, and pass sulphur dioxide gas into the mixture until almost all crystals are dissolved. The colour of the obtained solution is pale green.

A saturated aqueous solution of sodium metabisulphite, $Na_2S_2O_5$, can also be used, provided the salt has not been kept in air for a long time.

Place 2 ml of acetone and 3-4 ml of sodium bisulphite solution in a test tube. The reaction mixture gets slightly warm. Cool it in ice-cold water and shake the test tube, or rub its walls with a glass rod. A white precipitate of acetone bisulphite soon falls out. Separate it on a funnel with suction and dry on filter paper.

Treat part of the obtained substance in a test tube with hydrochloric acid by gently heating and feel the odour of the evolving gas. Heat the remainder with 1 ml of alkali solution; note the odour of the evolving vapours and try them for combustibility.

71
Reaction of Acetone with Sodium Sulphite

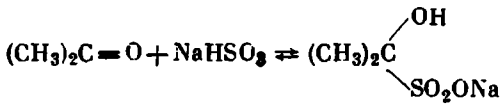
REAGENTS

Acetone, pure.
Sodium sulphite, 5-10 per cent solution.
Sulphuric acid, 0.1-0.2 *N* solution.

Add a drop of phenolphthalein to 1 ml of sodium sulphite solution. If pink colouration develops, remove it by adding carefully a few drops of dilute acid, avoiding its excess.

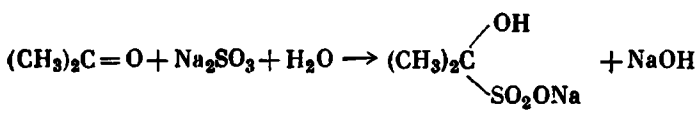
Place 1 ml of water and a drop of phenolphthalein into another test tube, and add 1-2 drops of acetone into both: the liquid in the former test tube turns intense red. This indicates that hydroxyl ion is present only in the mixture containing sodium sulphite.

Aldehydes and many ketones react with sodium bisulphite with liberation of heat to give bisulphite compounds, crystalline salts of alpha-oxysulphonic acid. For example, acetone reacts with sodium bisulphite as follows:



Bisulphite compounds readily dissolve in water. In solution they are present in equilibrium with the forming components, and addition of acids, which destroy the bisulphite, or of alkalis, which bind it, decomposes the bisulphite compound with liberation of a free aldehyde or ketone. The bisulphites are decomposed by heating as well. The ability of aldehydes and ketones to form bisulphites is often used for isolation and purification of aldehydes and ketones. Sulphur in the bisulphite compounds is in its hexavalent state. The course of formation of these compounds can therefore be followed quantitatively by titrating excess bisulphite with iodine.

Higher aliphatic and many aromatic ketones react with sodium bisulphite very slowly or do not react at all, whereas aldehydes and lower ketones, containing the $CH_3—CO—$ grouping, react even with sodium sulphite



Solutions of bisulphite compounds, and of free sodium bisulphite, react neutral to phenolphthalein. Alkaline reaction (Experiment 71)

indicates the formation of acetone bisulphite and can be utilized for quantitative (acidimetric) control of the reaction.

The formation of bisulphite compounds of aldehydes and ketones is the nucleophilic addition reaction (Experiment 68). Out of the two nucleophile ions, HSO_3^- and SO_3^{2-}, that attack the carbon of the carbonyl group, this is, perhaps, the SO_3^{2-} ion that is the agent, even if its concentration in the bisulphite solution is very low.

The free electron pair of the sulphur atom forms the C—S bond with the carbon of the carbonyl group that bears partial positive charge. The formal electronic state of sulphur atom changes from +4 to +6. The oxidation state characteristic is seldom applied to carbon atoms in organic compounds. In such a formal approach, the oxidation state of the carbon atom in the carbonyl group of aldehydes and ketones is 0, while in alcohols, the oxidation state of carbon bonded to the hydroxyl group is —2. The oxidation state of carbon atom bonded with the sulphur atom in alpha-oxysulphonic acids is also —2 (Experiments 70 and 71). Hence, one can assume that sulphur is oxidized and carbon reduced in these reactions.

72
Reaction of Acetone with Phosphorus Pentachloride (Preparing 2,2-Dichloropropane)

REAGENTS

Acetone, pure.
Phosphorus pentachloride, powder.

Use the HOOD.

Place 3 ml of acetone in a wide dry test tube and carefully add, in small portion, 10 g of phosphorus pentachloride weighed out onto a sheet of paper. Cool the test tube, preferably in water with snow or ice, and shake continuously. As soon as phosphorus pentachloride is all dissolved, transfer, with constantly shaking, the yellow solution thus obtained into a flask or a beaker containing 25 ml of water with pieces of ice or snow. The greater part of the reaction mixture is dissolved with liberation of heat, and drops of heavy liquid are formed on the bottom of the vessel.

Continue shaking for a few minutes, then allow the mixture to settle, decant the greater part of the acid aqueous layer, and pipette the insoluble oily product, 2,2-dichloropropane, into a test tube containing 3-4 ml of water. Add 0.5-1 ml of dilute alkali solution to neutralize acid admixtures, and shake the test tube.

The odour of pure 2,2-dichloropropane resembles that of chloroform. It can be used (as a representative of halogen-substituted fatty hydrocarbons) in Experiments offered in Chapter 5. The yield of the product is about 4 g.

Aldehydes and ketones readily react with phosphorus pentachloride, the carbonyl oxygen being replaced in this reaction by two chlorine atoms. Acetone gives 2,2-dichloropropane (b.p. 70 °C, density 1.1 g/cc):

$$(CH_3)_2C=O+PCl_5 \longrightarrow (CH_3)_2CCl_2+POCl_3$$

Phosphorus oxychloride, which is formed in this reaction (b.p. 107 °C, density 1.69 g/cc), is insoluble in water, but is easily hydrolysed in it:

$$POCl_3+3H_2O \longrightarrow 3HCl+H_3PO_4$$

Like the starting acetone, both acids are readily soluble in water. Excess phosphorus pentachloride, if any, vigorously reacts with water to give phosphorus oxychloride and hydrogen chloride. Thus, dichloropropane is the only reaction product insoluble in water and stable to water or aqueous solution of alkali in the cold.

73
Formation of Iodoform from Aldehydes and Ketones

REAGENTS

Acetone (see Experiment 67).
Acetaldehyde, solution (see Experiments 56, 57, 58).
Formaldehyde, solution (see Experiment 57).
Solutions of 1-2 drops of pure acetone, acetaldehyde, and formaldehyde in 1-2 ml of water can be used instead of the solutions obtained in the previous experiments.

Place 1-2 ml of dilute aqueous solution of a substance in question into a test tube, add 1 ml of iodine solution, and then a few drops of alkali solution until the colour vanishes. Yellow iodoform, having the specific odour, immediately precipitates from some solutions without heating.

Formation of iodoform from alcohols has been discussed in detail in Experiment 49. The process requires heating. The intermediate phase of the reaction is oxidation of alcohol to aldehyde or ketone. Formation of iodoform directly from aldehyde or ketone, whose molecule contains the CH_3—CO— grouping, is faster even at room

temperature, since the oxidation phase is omitted (see explanations to Experiment 69). The solubility of iodoform in water is negligibly small, and the reaction is therefore very sensitive and can be used, for example, for detecting very small concentrations (0.04 per cent) of acetone in water.

Formaldehyde molecule does not contain the atom grouping that is necessary for the formation of iodoform. For this reason formaldehyde is oxidized to formic acid in the conditions of the experiment. On the other hand, ethyl acetoacetate, $CH_3COCH_2COOC_2H_5$, and some other similar compounds, although they contain the $CH_3—CO—$ grouping, do not form iodoform. Under conditions of the experiment they are decomposed with liberation of acetic acid, the methyl group of which is not easily iodized.

CHAPTER EIGHT

CARBOXYLIC ACIDS AND OXYACIDS OF FATTY SERIES

Various fatty acids, most of which are quite readily available, can be used in experiments (Table 5). Solution of formic acid can easily be prepared during the laboratory work (see Experiment 80). Methacrylic acid (see Experiment 262) can also be used.

Table 5

Properties of Carboxylic Acids and Oxyacids of the Fatty Series

Acid	Formula	M. p., °C	B. p., °C	Density, g/cc
Formic acid	$HCOOH$	8	101	1.22
Acetic acid	CH_3COOH	17	118	1.05
Stearic acid	$C_{17}H_{35}COOH$	70	—	0.94
Trichloroacetic acid	CCl_3COOH	58	196	1.62
Oxalic acid	$HOOC-COOH \cdot 2H_2O$	101	—	—
Succinic acid	$HOOC-(CH_2)_2-COOH$	185	235	—
Oleic acid	$CH_3(CH_2)_7=CH(CH_2)_7COOH$	16	286 at 100 mm Hg	0.89
Fumaric acid	$HOOC-CH=CH-COOH$	~300	—	1.63
Lactic acid	$CH_3CH(OH)COOH$	18	122 at 15 mm Hg	1.24
Tartaric acid	$CH(OH)COOH$ $\vert$ $CH(OH)COOH$	170	—	—
Citric acid	$HO-C(CH_2COOH)(COOH)-CH_2COOH \cdot H_2O$	153	—	1.54

Formic, acetic, and lactic acids are very hygroscopic and crystallize only when they contain no water

Acetic acid can easily be prepared by heating a mixture of sodium acetate (calcium acetate or potassium acetate) with concentrated sulphuric or phosphoric acid in a flask provided with a gas outlet tube and a condenser. If the starting salt is anhydrous (see Experiment 23), acetic acid, distilled even with a small excess of a mineral acid, crystallizes at a temperature of 0 °C.

The properties and reactions of the acids, as well as of other compounds, should in many cases be studied by examining simultaneously several representatives of a given class: the relationships between the structure of an organic compound and its properties become then more vivid.

74
Solubility of Carboxylic Acids and Their Salts in Water

REAGENTS

Organic acids, e.g. *acetic*, *stearic*, *trichloroacetic*, *oxalic*, *succinic*, *lactic*, *tartaric* or *fumaric acid*.

Place a few drops, or crystals (about 0.05-0.1 g) of each acid in a test tube, add 1-2 ml of water, and shake. If the acid is not dissolved at room temperature, heat the mixture. Take approximately equal quantities of the acids and water for each parallel test.

Cool the mixtures and see whether or not the crystals that dissolved only on heating precipitate from the solution.

Use the obtained aqueous solutions of the acids in Experiments 75, 78 and 79.

In some test tubes, particles of sparingly soluble acids can remain in the mixture. Shake the suspension, transfer part of it into other test tubes, and add 2-3 drops of dilute alkali: the crystals dissolve on shaking.

Monobasic carboxylic acids whose molecules contain less than six carbon atoms usually readily dissolve in water. Formic, acetic, propionic and *n*-butyric acids are miscible with water in any proportion.

The solubility of acids in water usually increases with the number of the hydrophilic (carboxyl and hydroxyl) groups in the molecule, and the solubility decreases with increasing number of cabron atoms in the acid molecule (see explanations to Experiment 1).

Organic acids, as a rule, readily dissolve in caustic alkali solution to give salts.

75
Comparison of Ionization Degrees of Acids

REAGENTS

Organic acids, solutions (see previous Experiment).
Phenol, about 6 per cent saturated solution.
Glycerol, 5-10 per cent solution.
Congo red test papers.

To prepare test papers, soak filter paper in a 1 per cent solution of Congo red (an azo dye obtained by the combination of tetrazotized benzidine and naphthionic acid), dry it, and cut into strips.

Try the action of various acids of about the same concentration on the Congo-treated test paper. To do so, dip a clean thin rod into the acid and draw a line on the test paper: the colour of the lines and its intensity are different.

For the purpose of comparison, try the action of water, glycerol and phenol solutions, and also dilute hydrochloric (sulphuric) acid on the test paper in the same way.

Weak acids colour the Congo red test paper brownish black. Stronger acids colour it bluish black. The strongest acids produce a persistent blue colouration.

Arrange the tested acids in the order of their increasing acidity. Different concentrations of acid solutions can produce a certain effect on the position of the acids in this series.

The dissociation degree of a weak acid in a dilute solution is characterized by the ionization constant K and concentration of the acid solution C, in gram-equivalents per litre. Once the values of K and C are known, it is possible to determine approximately the degree of dissociation of acid α as a percentage in a given solution, as well as the concentration of hydrogen ion $[H^+]$ in the solution, in moles per litre. Most organic acids are weak electrolytes and these values can be found from the following formulas (derived from the law of mass action):

$$\alpha = \sqrt{K/C} \times 100; \quad [H^+] = \sqrt{KC}$$

For very weak acids, and for small concentrations, i.e. in cases where the product KC is close to 10^{-14}, it is necessary to introduce a correction for the hydrogen ion concentration in water. To that end, the ionic product of water K_w, whose magnitude at room temperature is close to 1×10^{-14}, should be incorporated into the for-

mula. The approximate hydrogen ion concentration in the solution can be found from the formula:

$$[H^+] = \sqrt{KC + K_w}$$

These formulas do not hold for strong acids, such as sulphuric, hydrochloric, or trichloroacetic.

Ionization constants of organic acids characterize their relative strength and strongly vary with the composition and structure of their molecule.

The ionization constants of acetic acid and its subsequent homologues are of the order of 1×10^{-5}-2×10^{-5}, i.e. the acids are comparatively weak. Formic acid is much stronger. Oxalic acid dissociation is greater than, for example, that of phosphoric acid, while trichloroacetic acid is stronger than many mineral acids.

The different 'strength', i.e. ionization degree of carboxylic acids, is explained by the effect of substitutes located sufficiently close to the carboxyl group or, to be more exact, by their inductive effects (*I*). Compared with the hydrogen atom at the carbon atom, the following substituting electrophilic groups show the $-I$ effect, i.e. draw the electron pairs of close carbon atoms: (H) < OH < Br < < Cl < COOR < CO < NO_2.

The members of this series are arranged in the order of their increasing inductive effect. This effect is transmitted further along the bonds of the carbon atom chain to the carboxyl group, and the easiness of ionization of its proton increases with the strength of the $-I$ effect of the substitute. The inductive effect of the hydrocarbon radicals is positive (also as compared with that of the hydrogen atom), i.e. the hydrocarbon radicals repulse the electron pair of the neighbouring carbon atom, and their presence somewhat decreases the acid strength.

The inductive effect rapidly weakens in the chain of ordinary C–C bonds. The stronger ionization of formic acid (compared with acetic acid) is explained not only by the $+I$ effect of the CH_3 group, but also by differences in solvation of these two acids in solution.

The ionization constants of some substances are given in Table 6. For polybasic acids only the ionization constant K_1 of the first carboxyl group is given. The second and subsequent carboxyl groups are ionized much weaker. The last columns of the table give the concentration of hydrogen ion in 0.1 *M* aqueous solutions of various acids (both absolute and relative as compared with the conventional unit concentration of hydrogen ion in acetic acid solution). The figures vividly illustrate the relative strength of acids in similar solutions.

The pH range of Congo red is from 3.0 (blue) to 5.0 (red), i.e. from 1×10^{-3} to 1×10^{-5}, in terms of the concentration of hydrogen ion (see Table 6).

Table 6

Ionization of Acids

Substance	Formula	Ionization constant, K_1	Concentration of hydrogen ion in 0.1 *M* aqueous solution ($C = 0.1$)	
			absolute, mole/litre	relative ($[H^+]$ for acetic acid is 1)
Water	HOH	1.8×10^{-16}	1×10^{-7}	0.00007
Glycerol	$C_3H_5(OH)_3$	7×10^{-15}	1.3×10^{-7}	0.0001
Phenol	C_6H_5OH	1.3×10^{-10}	3.6×10^{-6}	0.003
Formic acid	HCOOH	1.8×10^{-4}	4.25×10^{-3}	3.2
Acetic acid	CH_3COOH	1.8×10^{-5}	1.34×10^{-3}	1
Butyric acid	$CH_3CH_2CH_2COOH$	1.5×10^{-5}	1.22×10^{-3}	0.9
Chloroacetic acid	$CH_2ClCOOH$	1.6×10^{-3}	1.26×10^{-2}	9.4
Trichloroacetic acid	CCl_3COOH	1.3×10^{-1}	$\sim 1 \times 10^{-1}$	~ 75
Carbonic acid (as dissolved CO_2)	$CO(OH)_2$	4×10^{-7}	2×10^{-4}	0.15
Oxalic acid	HOOC—COOH	5×10^{-2}	7×10^{-2}	~ 50
Succinic acid	$HOOC-(CH_2)_2-COOH$	6.6×10^{-5}	2.6×10^{-3}	2
Maleic acid	CHCOOH ‖ CHCOOH	1×10^{-2}	3.2×10^{-2}	24
Fumaric acid	CHCOOH ‖ HOOCCH	1×10^{-3}	1×10^{-2}	7.5
Glycolic acid	$CH_2(OH)COOH$	1.5×10^{-4}	3.9×10^{-3}	2.9
Lactic acid	$CH_3CH(OH)COOH$	1.4×10^{-4}	3.7×10^{-3}	2.8
Tartaric acid	CH(OH)COOH ‖ CH(OH)COOH	1×10^{-3}	1×10^{-2}	7.5
Phosphoric acid	H_3PO_4	8×10^{-3}	2.8×10^{-2}	21
Hydrochloric acid	HCl	—	$\sim 1 \times 10^{-1}$	~ 75

The accuracy of determination with pH test paper is only to two units of the pH scale, and the picture is less vivid than with Congo red test paper.

Not only carboxylic acids, but also sulphonic acids and salts of many amines, some easily hydrolysing anhydrides, esters, and some phenols and nitrophenols give acid reaction to various indicators in aqueous or aqueous-alcoholic solution.

76
Displacement of Acids from Their Salts by Other Acids

REAGENTS

Acetic acid, dilute.
Oxalic acid, about 8 per cent saturated solution.
Sodium acetate, powder.
Sodium bicarbonate, powder.
Sodium succinate, concentrated solution.

To prepare the concentrated sodium succinate solution, mix 1 g of succinic acid with 3 ml of water, and add, in small drops, concentrated sodium hydroxide solution with shaking until the acid is all dissolved.

Place small samples of each salt (acetate, carbonate, and succinate) into separate test tubes and add a few drops of the organic acid in question and of dilute sulphuric acid (for the purpose of comparison).

Displacement of carbonic acid is revealed by liberation of carbon dioxide; of acetic acid, by the odour of the boiling mixture; and of succinic acid, by cloudiness or precipitation (immediately, or on standing for 5-10 minutes).

Weak acids (see Table 6) are displaced from their salts by stronger acids. The weak acid thus formed is decomposed with liberation of gas (as is the case with H_2CO_3), or is almost insoluble. In both cases the equilibrium is upset to facilitate revealing of the process.

Sulphonic acids, di-, and trinitrophenols, as well as other compounds having acid properties, displace carbon dioxide from bicarbonate solutions.

For studying acids sparingly soluble in water the method should be slightly modified (see Experiment 184).

77
Determining Equivalent Weight of Acid

REAGENTS

Succinic (tartaric) acid, dry powder. Other acids can also be used (see explanations below).
Sodium hydroxide, 0.1 *N* standard solution.

Weigh out about 0.2 g of acid in question to an accuracy of at least 0.001 g. Transfer the sample into a 50-100 ml beaker or conical flask, add 15-30 ml of water, 1-2 drops of phenolphthalein solu-

tion, and titrate the obtained mixture with the standard alkali by shaking until persistent pink colour develops.

Multiply the volume of alkali spent for titration by its normality factor to find the number of millilitres of an accurately uninormal solution and then find the equivalent weight of the acid:

$$E\,(\text{equiv.wt. of acid}) = \frac{\text{mass of sample in g} \times 1000}{\text{number of ml of } 1N \text{ alkali}}$$

The result can be checked by titrating a new acid sample.

Phenolphthalein, whose pH range is usually from 8.2 to 10.0, is normally more suitable for titration of weak organic acids than litmus or methyl orange. Sparingly soluble acids are titrated in alcohol or alcohol-benzene solution.

A *blank test* (titration with alkali solution of the same volume of the solvent containing the same number of drops of the indicator) should always be carried out, especially if mixed solvents are used. The correction obtained in the blank test should be introduced into the results of the calculations.

Example. A sample of a dibasic acid weighing 0.1150 g is dissolved in a mixture of alcohol and water. 19.5 ml of 0.1 *N* solution of NaOH were spent for titration with phenolphthalein. It follows that the taken weight of acid is equivalent to 1.95 ml of its normal solution, i.e. 1.95/1000 g-equiv

$$E = \frac{0.1150 \times 1000}{1.95} = 59.0$$

The equivalent weight E, the molecular mass of the acid M, and its basicity n are related to each other as $M = nE$. The acid in our example is dibasic ($n = 2$). Hence its molecular mass is $2 \times \times 59 = 118$ (succinic acid). Once the molecular mass is known (e.g. determined cryoscopically), it can be divided by the equivalent weight to determine basicity. Hydroxyl groups of oxyacids are not usually titrated in the described conditions.

78
Differences in Oxidability of Organic Acids

REAGENTS

Organic acids, e.g. *formic*, *acetic*, *oxalic*, *tartaric*, and *fumaric*.

Prepare aqueous solutions of organic acids. To do so, mix 0.05-0.1 g of acid with 1-2 ml of water (see Experiment 74). Add 1 ml of dilute sulphuric acid and potassium permanganate solution (drop by drop) to the prepared solutions of each acid. The difference in

oxidability of the acids is clearly manifested by the change of colour of the solutions: some of them change their colour immediately and some on standing.

Saturated monobasic acids of normal structure, except formic acid, are stable to oxidants. Impure acetic acid can contain substances that are oxidized and change the colour of potassium permanganate solution. Formic acid, which is also an aldehyde with respect to its structure, is readily oxidized with formation of carbon dioxide and water (see Experiment 81).

Oxalic acid, which can easily be converted into formic acid by eliminating CO_2, is also readily oxidized with potassium permanganate in an acid medium. The first portions of $KMnO_4$ react slowly at room temperature, but as the divalent manganese ion is accumulated in the solution, it catalyses the process of oxidation. Malonic acid is also readily oxidized. Other homologues of dibasic acids are more stable to oxidants.

The oxidability of oxyacids sharply increases with the number of hydroxyl groups in the molecule. But such acids as lactic, and especially tartaric and citric acids are oxidized with $KMnO_4$ at room temperature slower than formic and oxalic acids. The ion of divalent manganese accumulates in the solution and catalyses the oxidation. Oxyacids react with $KMnO_4$ to give keto acids, carbon dioxide, and other products.

Unsaturated acids are usually readily oxidized by $KMnO_4$, to splitting the acid molecule across its double bond (Experiment 19).

Acids are oxidized by potassium permanganate in an acid medium easier than in alkaline. For example, oxalic acid is stable to alkaline solution of $KMnO_4$.

79
Reaction of Oxyacids with Ferric Chloride

REAGENTS

Organic acids, e.g. *acetic*, *oxalic*, *citric*, *tartaric*, *lactic*.
Acid whey.

Before the experiment, add a few drops of saturated aqueous solution of phenol to ferric chloride solution until violet colour develops.

Use dilute aqueous solutions of the acids in this experiment (see Experiment 74). Place 1-2 ml samples of the acids and the whey into separate test tubes, and add 2-3 drops of ferric chloride solution, containing phenol, into each of them: a bright yellow colouration, sometimes with a greenish tint, develops in oxyacid solutions and in whey.

Ferric chloride reacts with some carboxylic acids (e.g. acetic acid) to give coloured colloid solutions or precipitates of basic salts. The salts are the product of hydrolysis of the corresponding salts of iron. They precipitate faster and more effectively if the reaction solution is first neutralized with alkali (Experiment 84) and then boiled. This reaction is more characteristic of alpha-oxyacids. They react with ferric chloride to give stabler complex salts of iron with simultaneous oxidation of the oxyacid and reduction of the Fe^{3+} ion to Fe^{2+} ion (cf. Experiment 168). The solution is coloured bright yellow without preliminary neutralization.

Some other compounds containing hydroxyl, for example, sugars, also react with ferric chloride to colour the solution yellow, although the hue is less intense than with alpha-oxyacids.

The starting solution of ferric chloride is brownish yellow. To ensure a more conspicuous change of colour, its violet solution containing iron phenolate should be used (Experiment 168). Alpha-oxyacid binds iron and destroys phenolate. The violet colour of the solution thus changes to yellow.

Acid whey reacts with ferric chloride in a similar way since it contains free lactic acid.

80
Preparing Formic Acid from Oxalic Acid

REAGENTS

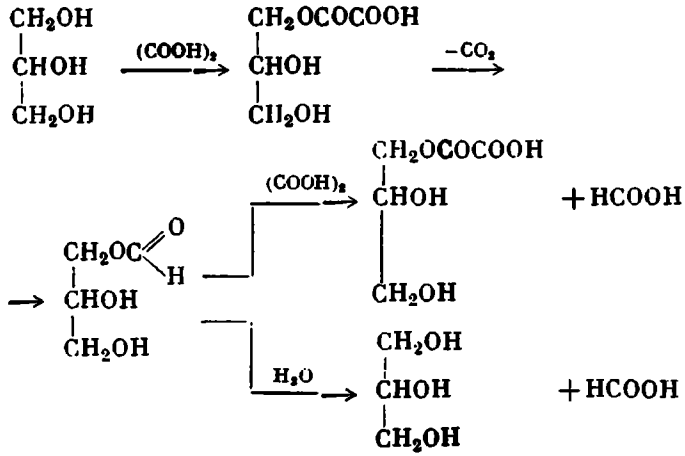
Oxalic acid, dihydrate, powder.
Glycerol.

Place 5 g of oxalic acid and 5 ml of glycerol into a wide test tube. Close it with a stopper through which a bent glass tube is passed. The length of the bent off end is 12-15 cm. Fix the test tube in an inclined position in the stand, and heat gently: oxalic acid dissolves, and ample quantities of gas begin evolving. As soon as the first drops of the distillate appear in the outlet tube, discontinue heating and add 2 g of oxalic acid into the test tube. Again connect the outlet tube and lower its end almost to the bottom of a receptacle containing 1-2 ml of water and cooled in a beaker filled with water. Continue heating the mixture seeing to it that the liquid does not splash out of the test tube, and collect the distillate (formic acid) in the receptacle. Continue the heating until the mixture of glycerol and oxalic acid becomes black. Dismantle the apparatus.

Use the collected formic acid (3-4 ml) in Experiments 81 and 82.

As a mixture of oxalic acid and glycerol is heated, glycerol monooxalate is first formed. With elimination of CO_2 it easily converts

into the formic acid ester, monoformin. Excess oxalic acid reacts with monoformin to give a volatile formic acid and again the oxalic acid ester. Simultaneously, monoformin is partly saponified by water contained in the mixture to give formic acid and glycerol. The reaction of glycerol with oxalic acid is as follows:



Formic acid and part of water are distilled off and the process is renewed. Thus, a small amount of glycerol promotes conversion of considerable amounts of oxalic acid into formic acid. Some side products, such as allyl alcohol, $CH_2=CHCH_2OH$, (b.p. 97 °C), are formed in the process.

81
Oxidation of Formic Acid

REAGENTS

Formic acid, pure (or prepared in the previous experiment).
Lime water or *baryta water*.

Place 0.5-1 ml of formic acid in a test tube provided with a gas outlet tube, and add 1 ml of dilute sulphuric acid and 1-2 ml of potassium permanganate. Lower the end of the outlet tube into another test tube (almost to the bottom) containing 1-2 ml of lime (baryta) water. Heat carefully the mixture to boiling.

The colour of $KMnO_4$ soon vanishes in the first test tube and a precipitate, or turbidity, appears in the second test tube as calcium carbonate (barium carbonate) is formed.

Formic acid, which is also an aldehyde, is readily oxidized (see Experiments 59-60) according to the equation:

$$H-COOH+O \longrightarrow HO-COOH \longrightarrow H_2O+CO_2$$

82
Decomposition of Mercuric Formate

REAGENTS

Formic acid.
Mercuric oxide, yellow; powder, or freshly precipitated paste.

Add a small quantity of mercuric oxide to a solution of a few drops of formic acid in 2 ml of water, and shake: mercuric oxide gradually dissolves. Freshly precipitated mercuric oxide dissolves momentarily.

Heat the clear solution on a boiling water bath or over a burner, with shaking at short intervals. Carbon dioxide is liberated energetically, and a white bulky precipitate of mercurous formate falls out in a few seconds. On further heating the precipitate turns grey: mercury metal is recovered. Free formic acid appears in the solution on heating (litmus test).

Mercuric formate, $(HCOO)_2Hg$, is readily soluble in water, and as its solution is heated, part of formic acid is oxidized to carbonic acid, whereas the salt is reduced to almost insoluble mercurous salt:

$$2(HCOO)_2Hg \longrightarrow (HCOO)_2Hg_2 + CO_2 + HCOOH$$

As the heating is continued, reduction proceeds to the formation of mercury metal:

$$(HCOO)_2Hg_2 \longrightarrow 2Hg + CO_2 + HCOOH$$

The reaction with mercuric formate is often used for identification of formic acid.

83
Decomposition of Formic Acid by Concentrated Sulphuric Acid

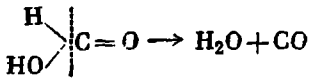
REAGENTS

Formic acid, anhydrous, or *sodium formate*, powder.

Mix 1 ml of concentrated sulphuric acid with 0.5 ml of formic acid, or 1 g of its salt, in a test tube provided with a flexible outlet tube. Collect carbon monoxide, which is liberated at room temperature or with slightly heating, over water in test tubes and burn. The colour of burning carbon monoxide is specifically blue.

If the reaction continues, light the gas at the orifice of the outlet tube to preclude accumulation of the noxious gas in the laboratory.

Carbon monoxide is formed from formic acid by elimination of water:



$$HCOOH \longrightarrow H_2O + CO$$

Sulphuric acid binds the formed water: both products are thus removed from the reaction.

84
Formation of Ferric Acetate and Its Hydrolysis

REAGENTS

Sodium acetate, crystalline.
Potassium ferrocyanide, 2 per cent solution.

Dissolve 0.1-0.2 g of sodium acetate in 2-3 ml of water in a test tube, and add 5-6 drops of ferric chloride solution with shaking: the liquid remains clear but turns brown red. Boil the solution for 1-2 minutes: reddish brown flakes precipitate. Discontinue heating, allow the mixture to stand, and carefully pipette a small quantity of the clear and colourless solution into another test tube. Add a few drops of potassium ferrocyanide (reagent for ferric ion) to the clear solution.

This experiment can be carried out with acetic acid as well. In this case, dissolve a few drops of acetic acid in 2-3 ml of water, thoroughly neutralize with alkali against litmus, and only then add ferric chloride.

Ferric chloride reacts with sodium acetate to give first ferric acetate, $(CH_3COO)_3Fe$ (by the usual exchange reaction), which is immediately hydrolysed to give a complex compound, chloride of basic ferric hexaacetate, $[Fe_3(OH)_2(CH_3COO)_6]^+Cl^-$. The formation of this complex compound accounts for the brown-red colouration of the solution. If the solution is boiled, the hydrolysis continues to quantitative precipitation of iron as insoluble basic ferric acetate:

$$Fe(CH_3COO)_3 + H_2O \longrightarrow CH_3COOH + Fe(CH_3COO)_2OH$$

This reaction is often used to remove ferric iron from solution. Formic and propionic acids give similar reactions with ferric chloride.

Polyhydric alcohols or oxyacids react with iron to give stabler complex compounds (see Experiments 51, 79, 90), and it becomes impossible to remove iron from solution by the action of sodium acetate in their presence.

85
Formation of Oxalate from Formate

REAGENTS

Sodium formate, powder.
Calcium chloride, 5 per cent solution.

Strongly heat about 1 g of sodium formate in a dry test tube over a burner. Put the flame of the burner to the mouth of the test tube: the issuing gas flashes with a specific blow characteristic of a mixture of hydrogen with air. After heating for a few minutes, allow the test tube to cool, add 3-4 ml of water, shake, and heat gently to accelerate dissolution. Filter the obtained solution.

Dissolve a small quantity of the starting sodium formate in another test tube.

Add a few drops of calcium chloride to both solutions: a white precipitate falls out in one test tube. The precipitate is insoluble in acetic acid and readily soluble in hydrochloric acid.

As sodium formate is heated to 400-450 °C, hydrogen is eliminated, and sodium oxalate is formed:

$$2HCOONa \longrightarrow H_2 + NaOOC-COONa$$

The oxalate can easily be detected by the action of calcium chloride, since unlike calcium formate, $(HCOO)_2Ca$, calcium oxalate, $(COO)_2Ca$, is insoluble in water.

When heated, formates of other metals undergo some other transformations. For example, zinc formate gives zinc carbonate and formaldehyde.

86
Thermal Decomposition of Oxalic Acid

REAGENTS

Oxalic acid, powder.
Lime (baryta) water.

Heat about 1-2 g of oxalic acid in a test tube with a gas outlet tube whose drawn end is lowered into another test tube containing 1-2 ml of lime water (baryta water). As soon as bubbling through the liquid in the receptacle becomes even and continuous (a precipitate falls out from lime water) withdraw the outlet tube from the liquid and light up the issuing gas at the orifice. The presence of carbon monoxide in the gas tinges the flame blue.

Crystalline oxalic acid, $C_2H_2O_4 \cdot 2H_2O$, first loses its water of crystallization. At temperatures above 100 °C the acid is partly sublimed to form an irritating mist. As carbon dioxide is eliminated, formic acid is formed, which in turn falls into water and carbon monoxide:

$$HOOC-COOH \longrightarrow CO_2 + HCOOH \longrightarrow CO_2 + CO + H_2O$$

Oxalic acid decomposes in a similar way at lower temperatures in the presence of concentrated sulphuric acid (cf. Experiment 83).

Dicarboxylic acids, containing the carboxyl groups at the same carbon atom, comparatively readily convert on heating into monocarboxylic acids (decarboxylation reaction):

$$RCH(COOH)_2 \longrightarrow RCH_2COOH + CO_2$$

If the carboxyl groups are remoted from one another, dibasic acids are heated with elimination of water and formation of cyclic anhydrides. Monobasic carboxylic acids can also be decarboxylated, but at higher temperatures:

$$RCOOH \longrightarrow RH + CO_2$$

Hydrocarbons are formed in this reaction.

87
Decomposition of Lactic Acid by Concentrated Sulphuric Acid

REAGENTS

Lactic acid.

Carefully heat a mixture of equal volumes (0.5-1 ml) of lactic acid and concentrated sulphuric acid in a test tube. Collect carbon monoxide issuing from the gas outlet tube over water in test tubes. Light up the gas first in the test tubes and then at the outlet tube orifice (cf. Experiment 83).

88
Oxidation of Lactic Acid in Acid Medium

REAGENTS

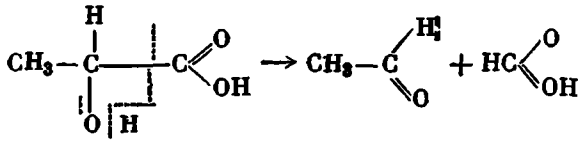
Lactic acid.

Place 0.5-1 ml of lactic acid in a test tube provided with a gas outlet tube, and add an equal volume of dilute sulphuric acid and 1-2 ml of potassium permanganate solution. Fix the test tube in

the stand in an inclined position, and lower the end of the gas outlet tube into a receptacle containing 1-2 ml of water and cooled in a beaker filled with water. Carefully heat the mixture almost to boiling: the mixture is quickly decolourized. The evolving gas passes into water in the receptacle. Heat for a few minutes and then dismantle the apparatus.

The solution of volatile reaction products in the receptacle has the odour of acetaldehyde and gives reactions characteristic of aldehydes.

When heated, especially in an acid medium, lactic acid easily falls into formic acid and acetaldehyde:



Decomposition with formation of formic acid and aldehyde or ketone is characteristic of alpha-oxyacids.

In the presence of concentrated sulphuric acid, formic acid gives carbon monoxide (see Experiment 83), whereas acetaldehyde is polymerized into paraldehyde. Among the products of decomposition of lactic acid in an acid medium, formic acid is the first to be oxidized with permanganate to give carbon dioxide (see Experiments 78 and 81), whereas aldehyde, which is liberated in the presence of dilute sulphuric acid predominantly in the form of a monomer, partly passes into a receptacle.

In an alkaline medium, lactic acid is oxidized with $KMnO_4$ to pyruvic acid, $CH_3COCOOH$, without breaking the C—C bond.

89
Formation of Acid and Neutral Potassium Tartrates

REAGENTS

Tartaric acid, 5-7 per cent solution.
Potassium hydroxide, about 0.5 *N* solution.

Place 1 ml of tartaric acid and a drop of phenolphthalein into a test tube and add, from a burette, potassium hydroxide solution. Add the alkali drop by drop, with constantly shaking the test tube. Ample crystalline precipitate very soon falls out, the mixture still reacting acid. As alkali is further added, the precipitate gradually dissolves and when the mixture reacts alkaline, it dissolves completely.

Transfer part of the solution into another test tube and add, drop by drop, dilute sulphuric acid: the precipitate (or turbidity) appears again, and disappears on further addition of the acid.

Keep the remaining slightly alkaline solution of neutral tartrate for Experiment 90.

As the dibasic tartaric acid is neutralized, first an acid, and then a neutral salt are formed

$$\begin{array}{l}\mathrm{CH(OH)COOH} \\ \mathrm{CH(OH)COOH}\end{array} \xrightarrow{\mathrm{KOH}} \begin{array}{l}\mathrm{CH(OH)COOK} \\ \mathrm{CH(OH)COOH}\end{array} \xrightarrow{\mathrm{KOH}} \begin{array}{l}\mathrm{CH(OH)COOK} \\ \mathrm{CH(OH)COOK}\end{array}$$

Many tartrates are readily soluble in water. Potassium acid tartrate is only sparingly soluble.

The solubility of tartaric acid, potassium bitartrate, and potassium tartrate in 100 g of water at normal temperature is 138 g, 0.65 g, and 158 g, respectively.

Some other dibasic acids, e.g. oxalic acid, also form sparingly soluble acid salts of potassium, but the difference in solubility is, in these cases, less marked.

90
Reaction of Tartrate with Copper Hydroxide

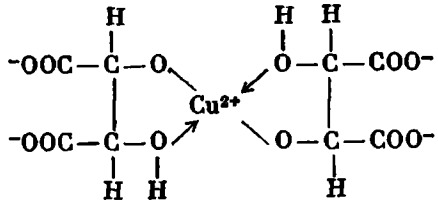
REAGENTS

Potassium (sodium) tartrate, 3-5 per cent solution, for instance, prepared in the previous experiment.

Place blue vitriol into a test tube and add a small excess of dilute alkali solution: blue copper hydroxide precipitates. Add a solution of potassium (sodium) tartrate: copper hydroxide dissolves to give a clear dark blue solution.

A molecule of the tartrate contains two adjacent hydroxyl groups containing relatively mobile hydrogen atoms. The tartrate therefore reacts with copper hydroxide in an alkaline medium to give soluble copper complexes, derivatives of the type of alcoholates of polyhydric alcohols (see Experiment 51). These compounds containing divalent copper easily oxidize many aldehydes and sugars (see Experiment 126) to precipitate cuprous oxide, and partly metallic copper. This reaction is used to determine sugar. Potassium-sodium tartrate (Seignette salt) is mostly used for the purpose. It is a consti-

tuent part of the Fehling solution (see Experiment 126) that contains K^+ and Na^+ ions and the complex anion



in an alkaline medium.

Heavy metals, such as Fe and Pb, form similar compounds.

Monovalent copper does not form this complex with tartrate.

91
Decomposition of Citric Acid by Concentrated Sulphuric Acid

REAGENTS

Citric acid, powder.
Lime water, or *baryta water*.

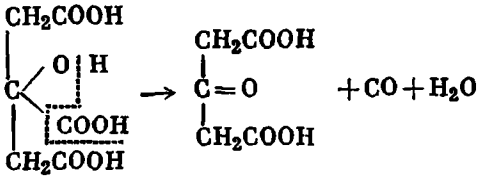
Place 1 g of citric acid into a test tube provided with a gas outlet tube and add 2 ml of concentrated sulphuric acid.

Fix the test tube in an inclined position. Take two other test tubes and fill 2-3 ml of clear lime (baryta) water into one of them (A), and the same volume of iodine solution with a few drops of alkali solution (to almost complete disappearance of the iodine colour) into the other test tube (B).

Carefully heat a mixture of citric and sulphuric acids over a burner: the mass begins foaming. Put the burner flame to the orifice of the gas outlet tube: the issuing gas burns with a blue flame, characteristic of carbon monoxide. Without interrupting the heating, lower the gas outlet tube first into the liquid in test tube A (the liquid becomes cloudy and a carbonate precipitates), and then into test tube B (iodoform precipitates at room temperature, cf. Experiment 73).

The experiment shows that citric acid reacts with sulphuric acid to give three reaction products: carbon monoxide, carbon dioxide, and acetone. Titration with alkali (see Experiment 77) shows that citric acid is tribasic. Formation of formic acid and then carbon monoxide, and also simultaneous formation of acetone are characteristic of action of concentrated sulphuric acid on alpha-oxyacids (cf. Experiments 87 and 88).

The decomposition mechanism is as follows:



Acetonedicarboxylic (beta-ketoglutaric) acid is then decarboxylated to give acetone:

$$CO(CH_2COOH)_2 \longrightarrow CO(CH_3)_2 + 2CO_2$$

The comparison of all these data confirms the structure of citric acid.

92
Isomerization of Oleic Acid into Elaidic Acid

REAGENTS

Oleic acid.

Copper, 0.5-1 mm dia. wire.

Place 2 ml of oleic acid and a piece of copper wire (cleaned and pressed into a bundle), weighing about 0.1-0.2 g, into a test tube. Add 1 ml of concentrated nitric acid. Close the test tube with a stopper and shake carefully so that nitrogen oxides that are liberated in the reaction of copper with nitric acid are better absorbed in oleic acid. The test tube contents get hot. Open the test tube at intervals to release the pressure inside it. When the foaming caused by the liberation of the gas almost stops in a few minutes, stopper the test tube tightly and leave it in the stand.

In about an hour, the foam layer of oleic acid (over a blue water-acid layer) becomes thick or hard and remains in place when the test tube is turned upside down.

There are two geometrical (*cis-* and *trans-*) isomers of unsaturated oleic acid, $C_{17}H_{33}COOH$ (like for many other compounds with double bonds); ordinary liquid oleic acid is a *cis*-isomer:

$$\begin{matrix} \overline{CH}-(CH_2)_7COOH \\ \| \\ CH-(CH_2)_7CH_3 \end{matrix}$$

Nitrogen oxides catalyse isomerization of oleic acid into a more stable *trans*-isomer, solid elaidic acid (m.p. 51 °C).

$$\begin{matrix} & CH-(CH_2)_7COOH \\ & \| \\ CH_3(CH_2)_7-CH & \end{matrix}$$

Oleic acid, bound in glycerides, can also be isomerized into elaidic acid, whose glycerides melt at higher temperatures. Liquid fats, containing many glycerides of oleic acid (e.g. olive oil), therefore solidify, or strongly thicken, in the described conditions as well. The 'elaidic test' is characteristic of such non-drying oils. Drying oils, which contain mostly glycerides of linolic and linolenic acids, do not thicken in these conditions.

Nitrogen oxides can be obtained by the action of nitric acid on copper, mercury, or crystalline sodium nitrite.

Interconversions of oleic and elaidic acids were studied by A. A. Albitsky and A. M. Zaitsev. Zaitsev proved that oleic acid can be catalysed into elaidic not only with nitrogen oxides, but with sulphur dioxide as well; however more rigid conditions are then required (temperature of 200 °C and pressure).

CHAPTER NINE

ACID DERIVATIVES. FATS. SOAPS

Acetic acid esters should be prepared in the course of the experiments. Commercial acetyl chloride and acetic anhydride should be kept ready for use. The constants of some derivatives of acetic acid are given in Table 7. Experiments with fats require commonly used and readily available natural products. Soaps prepared in Experiments 99 and 100 can be used in further experiments with soap. Hydrolysis of methyl methacrylate is discussed in Experiment 262.

Table 7

Properties of Acetic Acid Derivatives

Substance	Formula	B. p., °C	Density, g/cc
Ethyl acetate	$CH_3COOC_2H_5$	77	0.90
Propyl acetate	$CH_3COOC_3H_7$	102	0.89
Isopropyl acetate	$CH_3COOC_3H_7$(iso)	98	0.88
Butyl acetate	$CH_3COOC_4H_9$	125	0.90
Isobutyl acetate	$CH_3COOC_4H_9$(iso)	121	0.88
Amyl acetate	$CH_3COOC_5H_{11}$	148	0.89
Isoamyl acetate	$CH_3COOC_5H_{11}$(iso)	145	0.87
Acetyl chloride	CH_3COCl	51	1.10
Acetic anhydride	$(CH_3CO)_2O$	140	1.08

93
Formation and Hydrolysis of Esters

REAGENTS

Ethyl alcohol and its homologues (see Table 3).
Sodium chloride, saturated solution.

A. Mix in two test tubes 2-ml portions of alcohol and glacial acetic acid. Add 0.5 ml of concentrated sulphuric acid into one of them. Shake the test tubes and keep them on a hot (60-70 °C) water bath

for 10 minutes seeing to it that the liquid in the test tubes does not boil.

Cool the test tubes in cold water and add 2 ml of water into each. Note the odour of the formed ester and assess the volumes of the supernatant ester layers in the test tubes. The interface between the ester and water layers becomes more apparent with carefully swinging the test tubes. Now add 3-ml portions of saturated sodium chloride solution to both test tubes and observe the changes in the volume of the ester layer.

B. Pipette approximately equal portions (6-8 drops) of alkyl acetate into three test tubes. Add 1-ml portions of water into each test tube, 1-2 drops of dilute sulphuric acid into the second, and 1-2 drops of concentrated alkali solution into the third test tube. Heat and shake simultaneously all the three test tubes on a hot (60-70 °C) water bath: note the differences in the rate at which the drops and the odour of the ester disappear.

94
Preparing Ethyl Acetate

REAGENTS

Ethyl alcohol, crude or rectified.

Place 4 ml of alcohol, 5 ml of glacial acetic acid, 0.5 ml of concentrated sulphuric acid, and a boiling stone into a wide test tube. Instal a 'cold-finger' condenser (Fig. 3) in a plug with a hole and heat the mixture on a water bath for 30 minutes. Replace the 'cold-finger' condenser by a long air-cooled straight-run condenser and lower its end in a receptacle cooled in water with snow.

Heat the reaction mixture on a boiling water bath to distil the volatile products into the receptacle. Wash the distillate with a 10 per cent soda solution (2 ml), remove the lower layer using a pipette, and dry the remaining product with calcium chloride (magnesium sulphate, sodium sulphate) for an hour. Distil the dry product. The ester distils almost completely within the range of temperature of 74-76 °C. The yield is 4.5-5 g.

95
Preparing Isoamyl Acetate

REAGENTS

Isoamyl alcohol.

Mix 3 ml of glacial acetic acid and 5 ml of isoamyl alcohol in a large tube and add 2 ml of concentrated sulphuric acid. Place the hot reaction mixture on a water bath (without a condenser) and heat for 20 minutes. Cool the test tube and transfer the darkened

liquid into 20 ml of water containing pieces of ice (snow). Separate the supernatant ester (see explanations to Experiment 3), wash it with soda solution, dry with magnesium (sodium) sulphate, and distil from the test tube provided with a gas outlet tube and a thermometer. Collect the fraction boiling out within the temperature range of 143-145 °C. The yield is 2.5-3 g. The ester has a specific fruity odour.

Esters of acetic acid can be obtained by reactions with other alcohols (C_3-C_5) in the conditions described in Experiments 94 and 95.

The regularities of esterification reaction (effect of acid and alcohol structure on the esterification rate and on the equilibrium) have been studied in detail by N. A. Menshutkin and his followers (mostly in 1877-1891).

The esterification reaction is reversible

$$RCO-OH+H-OR' \rightleftharpoons RCO-OR'+H_2O$$

i.e. the processes of esterification and of hydrolysis of the formed ester occur simultaneously. The equilibrium is attained very slowly in the absence of a catalyst.

An active catalyst for both reactions is the hydrogen ion. Sulphuric acid not only ensures the high concentration of hydrogen ion in the mixture, but (given sufficient quantity) it can also bind water formed in the esterification process, and shift the equilibrium in the direction of ester formation. Markownikoff was the first to propose the use of sulphuric acid in the preparation of esters of organic acids (1873).

The hydrogen ion introduced with sulphuric acid also accelerates hydrolysis of ester. Alkali accelerates the hydrolysis. It binds carboxylic acid formed in the hydrolysis (see Experiment 93).

The points where the molecules of carboxylic acid, primary alcohol, and their ester are split, have been accurately located by the isotope-exchange method (labelled-atom method). If an alcohol containing the heavy isotope of oxygen ^{18}O is used for esterification, the isotope completely passes into the formed ester. During hydrolysis of ester with water that contains heavy oxygen the latter passes only into the formed acid, and does not pass into the alcohol.

Finally, during esterification of an acid containing a traced (heavy) oxygen in the hydroxyl group, this oxygen is completely eliminated to form the water molecule.

The chemistry of the processes is as follows:

$$RCO\overset{|}{\underset{|}{-}}OH+H\left|{}^{18}O-R' \longrightarrow RCO-{}^{18}OR'+H_2O\right.$$

$$RCO\overset{|}{\underset{|}{-}}OR'+H\left|{}^{18}OH \longrightarrow RCO-{}^{18}OH+R'OH\right.$$

$$R-CO\left|-{}^{18}OH+H\right|-O-R' \longrightarrow R-COOR'+H_2-{}^{18}O$$

During esterification of a carboxylic acid in an acid medium, a transition complex is first formed with participation of a proton (hydrogen ion), which is then combined with the hydroxyl oxygen of the carboxyl group. This facilitates the attack of the nucleophile, the alcohol that loses the proton of the hydroxyl group, on the hydroxyl carbon. A molecule of ester is formed by this process, whereas the carboxyl oxygen that is already bonded to two hydrogen atoms gives water.

As an ester is hydrolysed in an acid medium, a transition reaction complex is also formed. The proton that attacks the ester oxygen, and the molecule of water, whose oxygen passes to the carbonyl carbon, are constituents of the complex. The proton remains in the alcohol molecule, and the hydroxyl group of water remains in the acid molecule, whereas the second hydrogen atom of water is eliminated in the form of a proton that enters the complex formed by the next molecule of the ester.

The solubility of ester in water is markedly lower than that of the starting acid and alcohol, which is explained by disappearance of free hydroxyl groups. Salting out (adding a salt to the solution) decreases the solubility of ester in water even more (cf. Experiment 38).

The solubility of ethyl acetate in water (8.6 g in 100 ml of water at 20 °C) decreases with rising temperature.

96
Reaction of Acetyl Chloride with Water and Alcohol

REAGENTS

Acetyl chloride.
Ethyl alcohol, rectified.
Sodium chloride.

A. Place 1 ml of cold water into a test tube and add 3-5 drops of acetyl chloride. The latter is insoluble in water and settles to the bottom. Shake the test tube contents: acetyl chloride is hydrolysed, its drops disappear, and the mixture becomes hot.

Cool the liquid (smelling of acetic acid), divide it into two parts. Add 1-2 drops of silver nitrate solution to one of them: the presence of chloride ion becomes manifest. Thoroughly neutralize the other part with dilute alkali against litmus and add a drop of ferric chloride solution: the solution turns red. Heat the solution: a precipitate falls out and the solution is decolourized, which is characteristic of acetates (see Experiment 84).

B. Place 1 ml of ethyl alcohol into a test tube and add slowly 1 ml of acetyl chloride with shaking and cooling in cold water.

Without interrupting the shaking and cooling, add 2 ml of water and carefully neutralize the acid liquid with dilute alkali until the solution reacts slightly alkaline. A pleasant odour of ethyl acetate appears, and its layer floats to the surface. If the ester is not separated, salt it out by adding common salt (powder) to saturation (cf. Experiment 38).

Higher homologues of ethyl alcohol (see Table 3) can be used in Experiment 96, B.

Take part of the supernatant layer by a pipette. The ester can be used in Experiment 93, B

The carbon atom in the group is bonded with quite electronegative oxygen and chlorine. The electron density is displaced towards these elements, and the carbon atom therefore takes on a clear partial positive charge ($+\delta$). This strongly facilitates its interaction with nucleophiles (the oxygen atoms of alcohol, water, or alkali).

Acid chlorides, as a rule, readily react with water and alcohols to eliminate hydrogen chloride:

$$RCOCl + HOR' \rightarrow RCOOR' + HCl$$

where R′ is a hydrocarbon radical or hydrogen.

Only primary and secondary alcohols readily take part in this reaction to give esters.

Acetyl chloride reacts with water to form acetic acid and with ethyl alcohol to give ethyl acetate. The reaction of acetyl chloride with alcohols, i.e. in a homogeneous medium, is more smooth than with water, in which the acid chloride is insoluble.

Acid chlorides having high molecular mass react slower with water and alcohols. The reaction can be accelerated by adding alkali and heating the mixture.

97
Reaction of Acetic Anhydride with Water and Alcohol

REAGENTS

Acetic anhydride.
Ethyl alcohol, rectified.
Sodium chloride.

A. Place 1 ml of water and 0.5-1 ml of acetic anhydride in a test tube. Shake it, first at room temperature, and then with heating to boiling. Note the moment when the heavy drops of the anhydride disappear as a result of hydrolysis.

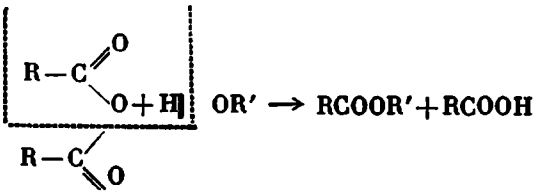
B. Place 1-ml portions of alcohol into two separate test tubes and add 1 ml of acetic anhydride into each. Heat one test tube until the liquid starts boiling, then cool it, and slowly add 2-3 ml of cold water. Note the liberation either of heavy drops of the starting anhydride or of a light layer of ethyl acetate. Add common salt: the layer separation becomes more apparent.

Using a pipette or a glass rod, add a drop of concentrated sulphuric acid into the other test tube. Shake the mixture and feel the test tube by the fingers: it becomes hot in 30-60 seconds. To prevent ebullition, cool the test tube in cold water. Wipe the test tube and allow it to become hot again. Immerse in water and cool. When liberation of heat stops, heat the test tube until the liquid starts boiling, cool, and add 2-3 ml of cold water and a little salt. Collect the supernatant ester and use it in Experiment 93, B.

Higher homologues of ethyl alcohol (see Table 3) can also be used in Experiment 97, B.

Anhydrides of carboxylic acids are usually insoluble in water. They react with water and alcohols much more slowly than acid chlorides. In Experiment 97, B, acetic anhydride does not completely react with alcohols even with heating in a homogeneous medium. The reaction rate sharply increases in the presence of a catalyst (concentrated sulphuric acid).

The reaction of anhydride with alcohols can be described as follows:



Thus, if acid anhydride is used to prepare esters, e.g. to acylate alcohol (substitution of the acid radical, *acyl* RCO—, for the hydroxyl hydrogen), only one out of the two acyl groups of the anhydride molecule is used, while the other group is converted into free acid.

98
Determining Saponification Equivalent

REAGENSS

Ester (any ester, e.g. those described in Experiments 94, 95, 259).
Alkali, standard, approximately 0.5 *N* solution in alcohol.
Hydrochloric acid, standard, approximately 0.3 *N* solution.

Alcoholic solution of alkali soon becomes yellow and resinified in storage. The solution should therefore be prepared immediately before the experiment. Act as follows: mix concentrated solution of potassium hydroxide (40 g of KOH in 50 ml of water), in a glass bottle provided with a rubber stopper, with alcohol (250 ml per 7-8 ml of alkali solution).

To standardize the alcoholic solution of alkali, fill it before the experiment into a burette with a clamp or a ball valve (do not use a burette with a glass stopcock), pipette 10-25 ml of hydrochloric acid of the known normality into a conical flask, and titrate (against phenolphthalein) with the alkali from the burette.

Saponify the ester in 100-150 ml conical flask. Instal a reflux condenser into the flask neck using a tight rubber stopper, or use a packing with a 'cold-finger' condenser with a stopper having a hole (Fig. 3).

Weigh out accurately (to the third decimal place) 0.4-0.7 g of the ester in a flask, add 20 ml of the standard alkali solution from the burette, connect the reflux condenser, and heat the mixture over a burner on a wire gauze, or on a water bath. Boil gently for 30-40 minutes, then cool the flask, add 2-3 drops of phenolphthalein solution and the standard acid from the other burette until the solution is decolourized. Back-titrate excess acid with the alkali solution in alcohol.

The saponification equivalent is the number of grams of ester that react with a gram-equivalent of alkali. Hence, the molecular mass of an ester can be determined by multiplying this equivalent by the number of saponified ester groups in a molecule (if the latter is known) (cf. Experiment 77). The saponification equivalent of monobasic acid esters is equal to the molecular mass of the ester.

Sum up the volume of the alkali solution added to the flask before boiling with the volume of alkali spent for back titration, and recalculate this total volume (by multiplying by correction factor of the alkali normality) into the number of millilitres of the accurately 1 *N* solution. Multiply the number of millilitres of the acid added to the flask by the normality factor. The result is the volume of the acid in millilitres of the accurately uninormal solution. Subtract the number of millilitres of the acid from the number of millilitres of the alkali. The difference is the number of millilitres of the normal alkali (*A*) spent for saponification of ester. The saponification equivalent of ester can be calculated from the formula:

$$\text{Saponification equivalent} = \frac{\text{ester sample in g} \times 1000}{A}$$

Example. The weight of ester sample is 0.620 g. The volume of the alkali ($K = 0.490$) added is 20 ml and that spent for back titration,

0.5 ml, i.e. 20.5 ml altogether, or 10.05 ml of 1 *N* solution. The volume of the acid ($K = 0.280$) added is 18.9 ml, or 5.28 ml as 1 *N* acid. The volume of 1 *N* alkali solution spent for saponification is

$A = 10.05 - 5.28 = 4.77$ ml

$$\text{Saponification equivalent} = \frac{0.620 \times 1000}{4.77} = 130$$

Most esters are saponified in the described conditions within 30 minutes. Boiling for longer time is seldom required.

99
Saponification of Fats with Alkali in Aqueous Solution

REAGENTS

Sunflower seed oil, or some other *liquid vegetable oil.*
Butterfat, animal fats.
Sodium chloride, saturated solution.
Congo test paper (see Experiment 75).
Ethyl alcohol, crude or hydrolysed.

The experiment should preferably be carried out with different fats simultaneously.

Place 3 g of fat and 6-7 ml of concentrated alkali solution in a small porcelain dish. Heat the mixture on a gauze over a burner, or on a sand bath, for 20-30 minutes until it starts gently boiling. Stir the mixture with a rod to prevent bumping. Add distilled water from time to time to maintain the initial volume of the mixture.

In 15-20 minutes, check for completeness of saponification. Accordingly, transfer a few drops of the mixture into a test tube, add 5-6 ml of distilled water (better hot water), and heat the solution with shaking on a water bath or over a burner. If the sample is all dissolved in water without liberating fat drops, the saponification can be considered complete. Otherwise continue heating the mixture for another few minutes. Check for completeness of saponification again.

On the termination of the saponification process, add 10-15 ml of hot saturated solution of common salt with stirring, then allow the mixture to settle and cool. A layer of soap floats to the surface of the aqueous solution. On cooling, the soap hardens. Separate the soap and keep for Experiments 101-104.

Add concentrated hydrochloric acid to the remaining aqueous solution. Add the acid by drops accurately to neutral reaction to congo. Pass the liquid through a small pleated filter wetted with water.

Evaporate the filtrate in a dish until crystallization starts. Now cool the mixture, add 5-10 ml of alcohol, and stir well. Decant the liquid, evaporate again to a syrup consistency, and test for the presence of glycerol (see Experiments 50 and 51).

100
Saponification of Fats with Alkali in Water-Alcohol Solution

REAGENTS

See Experiment 99.

Carry out parallel experiments with various fats.

Place 3 g of fat, 3 ml of alcohol, and 3 ml of concentrated alkali solution into a wide test tube and stir the mixture by shaking or using a glass rod. Heat the test tube on a water bath to boiling. The mixture is soon homogenized and saponification ends completely in 3-5 minutes. Test for completeness of saponification as instructed in Experiment 99.

Add a hot saturated solution of common salt to the obtained thick liquid with stirring: the liquid becomes cloudy and a layer of soap rises to the surface. Fill almost entire volume of the test tube with the salt solution to lift the salted-out soap layer to the test tube mouth. Allow the mixture to stand for a few minutes on a water bath, then transfer the test tube into a beaker containing cold water: the soap hardens in 5-10 minutes.

Remove the soap from the test tube using a glass rod or a spatula and keep for Experiments 101-104.

Detect the presence of glycerol in the remaining solution as instructed in Experiment 99.

All fats are esters of glycerol and various fatty acids. As a rule, fatty acids of natural fats contain an even number of carbon atoms, since they are synthesized naturally from two-carbon molecules of acetic acid. In making out the reaction equations for saponification of fats, various isomers containing residues of stearic, palmitic, and oleic acids in different quantities and positions can be depicted. The chemistry of fat saponification with alkali is as follows:

$$\begin{array}{l} CH_2O-COR \\ | \\ CHO-COR' \\ | \\ CH_2O-COR'' \end{array} + 3NaOH \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + RCOONa + R'COONa + R''COONa$$

Fat is insoluble in aqueous alkali and only gradually emulsified a soap is accumulated in solution (see Experiment 103). The saponification of fat with an aqueous solution of alkali is therefore a slow

process. But as alcohol is added, the mixture becomes homogeneous, the solubility of fat increases, and the reaction of saponification sharply accelerates.

The products of saponification of fats are glycerol and a mixture of salts of fatty acids, i.e. soap. They are soluble in water and in alcohol. Soap is dissolved in water to form a colloidal solution. Glycerol and alcohol are soluble in sodium chloride as well, whereas soap is insoluble and is therefore salted out from solution as a thick mass or clogs. Soap is salted out because of its decreasing dissociation in the presence of excess of one of the ions (Na^+) and because the hydrate shells are removed from the colloid particles of soap by the hydration of the added salt ions (cf. Experiment 38).

Saponification of fats with potassium hydroxide gives potassium soaps of softer consistency. Salting out with sodium chloride (exchange reaction) gives a mixture of sodium and potassium salts, the former being in prevalent quantities. Consistency of soaps also depends on the properties of the starting fat: liquid oils and fats give softer soaps.

The salting-out process is used in the manufacture of high-quality soaps. If the aqueous solution obtained by saponification is not salted out, it hardens into soap containing also glycerol, alkali, and large quantities of water.

If a solution, from which soap is salted out and its greater part removed, is acidified, fatty acids are separated from residual quantities of soap contained in the solution (see Experiment 104). The acids are non-wettable with water and are therefore retained on a wet filter paper.

Coloured soluble alcoholates of copper, which are characteristic of glycerol and other polyhydric alcohols, are formed in a slightly alkaline solution (Experiment 51). Excess acid should therefore be avoided in neutralization of soap solutions.

101
Solubility and Exchange Reactions of Soaps

REAGENTS

Soap (obtained in Experiment 99 or 100).
Calcium sulphate, saturated 0.2 per cent solution.
Lead acetate, 2-3 per cent solution.

A. Place 0.1-0.2 g of soap into two separate test tubes and add distilled water: 1 ml into one test tube and 6-8 ml into the other. Heat the test tubes and shake them: soap dissolves in both. Cool the test tubes in a beaker with cold water.

A more concentrated soap solution forms a dense jelly-like mass, while the dilute solution remains liquid and foams on shaking.

Soaps prepared from vegetable oil or butterfat dissolve in water more readily than soaps prepared from fats.

B. Divide the slightly opalescing dilute soap solution into three parts. Add an equal quantity of tap water to the first one, of calcium sulphate to the second, and of lead acetate to the third portion. White calcium and lead soaps precipitate in the latter two solutions. Depending on hardness, tap water produces cloudiness or precipitates flakes of calcium and magnesium soaps. Unlike the starting soap solution, all supernatant liquids almost do not produce lather on shaking.

Sodium and potassium salts of higher fatty acids are readily soluble in hot and with greater difficulty in cold water. The colloid nature of the formed solutions shows itself in opalescence of dilute solutions and formation of gel on cooling of concentrated solutions.

Calcium, magnesium, and lead salts of these acids are formed by the exchange reactions:

$$2RCOONa + CaSO_4 \longrightarrow (RCOO)_2Ca + Na_2SO_4$$

They are significantly less soluble in water and immediately precipitate; hence soap does not produce lather in hard water.

102
Hydrolysis of Soap

REAGENTS

Soap (prepared in Experiments 99 and 100)
Sodium chloride, saturated solution.
Ethyl alcohol, rectified.

Dissolve about 0.5 g of hard soap, obtained by salting out, in 4-5 ml of distilled water with heating, and salt out again with a hot saturated solution of common salt (see Experiment 100). Allow the supernatant layer of soap to harden, transfer it onto a filter paper, and dry.

Place a piece of the purified soap into a dry test tube, add 1-2 ml of alcohol, shake, and add 1-2 drops of phenolphthalein. Carefully transfer the liquid, pouring it by the wall, into another test tube containing 3-5 ml of water and note the colour change at the interface.

In repeated dissolution and salting out, soap is freed from the greater part of its impurities, from excess alkali in particular. The solution of soap in alcohol is only slightly ionized, and remains colourless, or is only slightly coloured by the addition of phenolphthalein.

Dilution of the alcoholic solution increases the ionization and hydrolysis of soap with formation of low-dissociated fatty acids:

$$RCOONa \rightleftharpoons RCOO^- + Na^+$$
$$RCOO^- + HOH \longrightarrow RCOOH + OH^-$$

Phenolphthalein detects excess hydroxyl ions in the solution.

103
Emulsifying and Washing Properties of Soap

REAGENTS

Soap (obtained in Experiments 99 or 100).
Liquid oil, e.g. sunflower seed oil, or kerosene.
Carbon black.

Heat and shake 0.1-0.2 g of soap with 6-8 ml of distilled water. Cool, and use the dilute solution of soap in the following experiments.

A. Place 1-2 drops of liquid oil into two test tubes, and add 2 ml of water into one and 2 ml of soap solution into the other test tube. Strongly shake both test tubes to obtain an emulsion of the oil. Fix the test tubes in the stand.

The emulsion in pure water contains rather large droplets of oil that soon separate on standing. The emulsion containing soap looks like milk; it contains minutest droplets of oil and is much stabler.

B. Place 8-10 ml of water and a small quantity of carbon black in a test tube and shake strongly. Pass the obtained fine suspension through a paper filter. Remove the filter from the funnel, unfold it and fold again so that its internal surface carrying the carbon black particles becomes external, and place the filter into the funnel. Pass a few millilitres of pure water through the filter into a clean test tube (or a beaker). Now transfer the funnel into another receptacle and pass a few millilitres of soap solution. The former filtrate is clear, whereas the latter contains many particles of carbon black.

Soap is a surface active agent (surfactant). Adsorbed on the interface of its solution with air or oil, it sharply reduces the surface tension. The stability of a lather or emulsion is thus strongly increased. The hydrophilic carboxyl groups of soap molecules at the interface are in the aqueous phase, whereas hydrophobic hydrocarbon radicals are oriented towards air, and when brought into contact with oil or fat, are partly dissolved in them to split them into fine droplets (emulsification). This accounts for the degreasing power of soap solutions in water.

The washing properties of soap solutions (manifested in the experiment with carbon black) are also explained by the adsorption of soap on carbon black particles. Here soap performs the role of a protective colloid and peptizes carbon black, i.e. prevents aggregation of its particles and disperses carbon black clots.

104
Isolation of Fatty Acids from Soap

REAGENTS

Soap (obtained in Experiments 99 or 100).
Sodium hydroxide, or *potassium hydroxide*, about 0.1 *N* solution.

A. Dissolve with heating about 1 g of salted-out soap in a test tube in 5-6 ml of distilled water. Add 3-4 ml of dilute sulphuric acid and place the test tube in a boiling water bath so that the level of the acidified and cloudy liquid is below the water level in the bath. The free fatty acids float to the surface to form a liquid layer. The aqueous solution becomes clear. As soon as the phase separation is complete, remove the test tube from the bath, add water to lift the layer of the fatty acids almost to the test tube mouth, and put the test tube into a beaker filled with cold water.

Fatty acids recovered from sunflower seed oil are almost odourless and remain liquid on cooling. Only a small precipitate falls out. Acids isolated from butterfat form a soft mass with a specific odour of rancid butter. Acids recovered from fats solidify. They have a faint odour.

B. Transfer acids isolated from butterfat into a test tube provided with an outlet tube. Add 5-7 ml of water, drop a boiling stone, and distil 2-3 ml of the liquid into a receptacle cooled in a beaker filled with water. The distillation is smooth, without bumping. The distillate is as a rule cloudy. Its odour is stronger than that of acids in the distillation test tube. Add a drop of phenolphthalein and 0.2-0.4 ml of alkali, drop by drop, until the solution turns crimson.

Most acids contained in butterfat are high boiling and not distilled with steam; in the conditions of the experiment they remain in the distillation test tube.

Solid animal fats contain mainly mixed and simple glycerides of higher saturated fatty acids: palmitic acid, $C_{15}H_{31}COOH$, and stearic acid, $C_{17}H_{35}COOH$, and small quantities of glycerides of unsaturated oleic acid, $C_{17}H_{33}COOH$. Butterfat is characterized by the presence of small quantities (less than 10 per cent) of glycerides of lower fatty acids: butyric acid, C_3H_7COOH, caproic acid, $C_5H_{11}COOH$, caprylic acid, $C_7H_{15}COOH$, and capric acid, $C_9H_{19}COOH$.

Liquid vegetable oils contain mainly glycerides of unsaturated acids. These are oleic acid, $C_{17}H_{33}COOH$, linoleic acid, $C_{17}H_{31}COOH$, and linolenic acid, $C_{17}H_{29}COOH$; at room temperature they are liquid. Linoleic acid was studied by A. N. Reformatsky in 1889, and linolenic acid was recovered from linseed oil by S. A. Fokin in 1902. Liquid oils contain glycerides of palmitic and stearic acids in the quantity not exceeding 25 per cent.

Lower fatty acids are distilled with steam. Their presence in the distillate can be detected by odour and acid reaction.

One of the methods to study the composition of fats is titration with alkali of the whole distillate or of its successive fractions.

Almost all acids composing fats and oils are monobasic. Their mean molecular mass can be determined by titrating the samples isolated in Experiment 104, A with alkali in an aqueous-alcoholic or alcohol-benzene solution (see Experiment 77).

105
Determining Unsaturatedness of Fats

REAGENTS

Fat.
Butterfat, boiled.
Vegetable oil.
Carbon tetrachloride, or *chloroform.*

Carry out simultaneously experiments with various fats. Melt solid fats before the experiment.

Dissolve a drop of each fat in 1 ml of carbon tetrachloride in a dry test tube. Add, from a burette provided with a glass stopcock, or from a graduated pipette, bromine and shake. Stop adding bromine when the solution colour persists.

Compare the volumes of bromine spent to attain the same pale orange colour of various fats. Arrange the fats in the order of their increasing unsaturatedness.

The degree of unsaturation of fats, which is due to the presence of glycerides of acids containing double bonds (see Experiment 104), can be assessed by the addition of halogens — bromine (cf. Experiment 18) or iodine. The assessment can be both qualitative and quantitative. These data, obtained by more accurate methods, are very important for assessing properties of fats.

106
Formation of Acrolein by Decomposition of Fat

REAGENTS

Fat, vegetable or animal.
Potassium (*sodium*) *bisulphate*, powder, (see Experiment 50).

Place about 0.5 g of bisulphate and a drop of liquid fat (or a piece of solid fat) into a dry test tube. Shake the tube and heat slightly to mix the components. Now heat the mixture over a burner holding the test tube horizontally. The mixture blackens, steam and other volatile products, having the pungent and specific odour of acrolein, are evolved.

Thermal decomposition of fats gives a complicate mixture of products, comprising also glycerol, the esters of which are fats. In the presence of dehydrating agents (bisulphates of potassium or sodium in particular) glycerol turns into acrolein (see Experiment 50) easier than by heating fats without dehydrating agents.

NITROGENOUS COMPOUNDS OF FATTY SERIES

Table 8 gives compounds that should be used in experiments offered in this chapter.

Almost all these substances are prepared in the course of the experiments. Urea and glycine should be kept ready for use.

Table 8

Properties of Fatty Nitrogenous Compounds

Substance	Formula	M. p., °C	B. p., °C
Nitromethane	CH_3NO_2	—28	101
Methylamine	CH_3NH_2	—93	—7
Dimethylamine	$(CH_3)_2NH$	—96	7
Trimethylamine	$(CH_3)_3N$	—117	3
Tetramethylammonium iodide	$(CH_3)_4NI$	Decomposes above 230 °C	—
Ethylamine	$C_2H_5NH_2$	—81	17
Diethylamine	$(C_2H_5)_2NH$	—50	56
Triethylamine	$(C_2H_5)_3N$	—115	89
Tetraethylammonium iodide	$(C_2H_5)_4NI$	200	—
Acetamide	CH_3CONH_2	81	222
Urea	NH_2CONH_2	133	decomposes
Glycine	NH_2CH_2COOH	290 decomposes	—

107
Preparing Nitromethane

REAGENTS

Chloroacetic acid.
Sodium bicarbonate, powder.
Sodium nitrite.

Weigh out 5 g of chloroacetic acid into a small beaker, and add 10 g of snow or crushed ice. Place the beaker into ice-cold water and gradually add 5 g of sodium bicarbonate with thoroughly stirring the

foaming mixture with a glass rod. As soon as the entire carbon dioxide has evolved, add a solution of 10 g of sodium nitrite in 6 ml of water, and stir again. Transfer the liquid from the beaker into a large test tube or a round-bottomed flask (the liquid volume should not exceed half volume of the flask), and drop a boiling stone. Fix the vessel in the inclined position in the stand, insert a plug with an outlet tube, and connect a long descending air-cooled condenser. Use a test tube cooled in water as a receptacle.

Heat the reaction mixture over a burner, first gently and then stronger. The liquid gradually blackens and foams (liberation of carbon dioxide). Water and heavy colourless oil are distilled. Discontinue distillation when oil-free water drips into the receptacle.

Separate the nitromethane and use without purification in Experiment 108. The yield is about 1.5 g.

To purify the product, dry it with calcium chloride and distil.

Chloroacetic acid is neutralized by sodium bicarbonate at room temperature:

$$ClCH_2COOH + NaHCO_3 \longrightarrow ClCH_2COONa + CO_2 + H_2O$$

The reaction mixture should be cooled to prevent hydrolysis, i.e. substitution of hydroxyl group for chlorine with formation of glycolic acid. Further reaction of sodium chloroacetate with sodium nitrite with heating replaces chlorine by the nitro group to give the nitroacetate:

$$ClCH_2COONa \xrightarrow{+NaNO_2} NaOOC-CH_2NO_2$$

The chemistry of the reaction is very complicate. The formal electronic state of the nitrogen atom changes from +3 to +5 because of the formation of the N—C bond from the free electron pair of the nitrogen atom, instead of the electron pair that is lost with the negative chloride ion (see also explanations to Experiments 70 and 71).

The nitroacetate is then hydrolysed to give nitromethane:

$$NO_2CH_2COONa + H_2O \longrightarrow CH_3NO_2 + NaHCO_3$$

Some other, more complicate conversions occur simultaneously, and the yield of nitromethane does not therefore exceed 30-40 per cent of theory. The density of nitromethane is 1.14 g/cc.

108
Reactions of Nitromethane

REAGENTS

Nitromethane (see Experiment 107).
Sodium hydroxide, about 0.1 *N* solution.
Sodium nitrite.
Zinc, granulated.
Ethyl ether.

A. Place a few drops of nitromethane in a test tube and add water, drop by drop, with shaking until the product is all dissolved. Test the reaction of the solution by litmus paper. Add a drop of phenolphthalein and then, slowly, drop by drop, 0.1 *N* alkali solution until the red colour persists.

Add a few drops of ferric chloride solution and 1-2 ml of ether and shake: the reaction product passes into the ether layer.

B. Mix a few drops of nitromethane with 1 ml of water and 2-3 drops of concentrated alkali solution. Cool the obtained clear liquid in water or snow, add 0.5-1 ml of sodium nitrite and then, drop by drop, dilute sulphuric acid until red-orange colour develops and then vanishes. As alkali is added, the colouration is restored.

C. Dissolve a few drops of nitromethane in 1-2 ml of concentrated alkali solution, add 2-3 grains of zinc, and heat the mixture. Note the specific odour and put a wet red litmus paper to the mouth of the test tube: it turns blue.

The nitrogen atom of the nitro group NO_2 bears the full positive charge, and each oxygen atom bears half the negative charge of the electron. The nitro group is therefore a strong electron acceptor and produces a clear $-I$ inductive effect in an organic molecule. For example, it is characterized by special mobility, protonization, of hydrogen atoms at the carbon atom to which the nitro group is bonded (Experiments A and B; see also Experiments 63 and 75, and explanations to them). As a result, like all primary and secondary nitro compounds, practically neutral nitromethane is a pseudo acid, i.e. displays tautomerism:

$$CH_3NO_2 \rightleftharpoons CH_2{=}NOOH$$

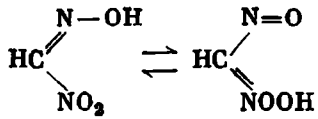
Isonitro compound (a nitro compound containing the group =NOOH) is a strong acid (*aci-nitro* compound). Alkali binds this acid to shift the equilibrium in the direction of formation of the isoform. The sodium salt of nitromethane, $CH_2{=}NOONa$, reacts with ferric chloride to give a complex iron salt, which is intensely coloured and, like ferric thiocyanate (see Experiment 53), is soluble in ether. This reaction is characteristic of primary and secondary nitro com-

pounds. It was proposed by M. I. Konovalov in 1895 and studied in detail by S. S. Nametkin. The classical works of the Russian scientists laid foundation for the modern methods of synthesis and use of nitro derivatives of saturated hydrocarbons and cycloparaffins.

Nitromethane salt reacts with nitrous acid to give a brightly coloured salt of methylnitrolic acid:

$$H_2C{=}NOONa + HONO \rightleftharpoons H_2O + ONHC{=}NOONa$$

Free methylnitrolic acid, like nitromethane, shows tautomerism. In neutral and acid solutions it is colourless:



Alkalizing shifts the equilibrium to the formation of a coloured salt in the aci-form. This colour reaction is only characteristic of primary nitro compounds.

Nitromethane is reduced in an alkaline solution to give free gas methylamine (cf. Experiment 202).

109
Formation and Properties of Fatty Amines

REAGENTS

Methyl iodide (see Experiment 28).
Ethyl iodide (see Experiment 29).
Ammonia, saturated solution in methyl or ethyl alcohol.
Picric acid, saturated solution (see Experiment 117).

Prepare ammonia solutions as follows. Place 10-15 g of solid alkali (KOH or NaOH) in a flask provided with an outlet tube and a dropping funnel, and add, drop by drop, concentrated aqueous ammonia. Connect a soda lime tube to the gas outlet tube. The liberated gaseous ammonia passes through the soda lime tube into a mixture of 5 ml of methyl alcohol and 0.4 ml of water (or 5 ml of ethyl alcohol and 0.2 ml of water). The mixture is contained in a test tube cooled to a temperature of 0 °C. The flow-rate of ammonia should be rather high. The saturation should continue for 10-20 minutes: the volume of the liquid in the receptacle should considerably increase during this time. Carry out this operation in the HOOD.

A. Place the cold solution of ammonia in methyl alcohol in a test tube, add 1 ml of methyl iodide, tightly close with a rubber plug, shake, and allow to stand at 0 °C. White crystals of the quaternary

salt of ammonia soon precipitate. Filter the salt with suction in 10-20 minutes (Fig. 6), wash with 1-2 ml of methyl alcohol, and keep for Experiment 110. Evaporate the filtrate in a dish on a water bath to 2-3 ml, add 5 ml of water, and evaporate again to 2-3 ml. Use the alcohol-free solution in Experiments C and D.

B. Place ammonia solution in ethyl alcohol in a test tube, add 1.5 ml of ethyl iodide, close the test tube with a stopper, shake, and keep at 0 °C for an hour. Evaporate the clear liquid in a dish on a water bath to 1/5th initial volume and cool: crystals precipitate. Filter the crystals with suction and keep for Experiment 110. Add 5 ml of water to the filtrate, evaporate to 2-3 ml, and use the liquid together with the precipitate in Experiments C and D.

C. Mix part of the solution of amine salt obtained in A or B with an equal volume of water, determine the reaction to phenolphthalein, and add 1 ml of concentrated alkali solution. Heat the mixture to boiling. The evolving gas colours a wet red litmus paper blue. The odour of the gas resembles that of ammonia. Unlike ammonia, the gas is combustible. Close the test tube with a plug provided with a gas outlet tube and light up the issuing gas: the gas burns for a considerable time (provided the liquid in the test tube boils).

D. Add three volumes of saturated aqueous solution of picric acid to the remaining parts of the solutions (Experiments A and B), and place the test tubes in cold water or snow. A mixture of picrates soon precipitates in the form of yellow crystals.

110
Formation of Quaternary Bases of Ammonia

REAGENTS

Tetramethylammonium iodide (see Experiment 109).
Tetraethylammonium iodide (see Experiment 109).
Silver oxide, damp.

To prepare silver oxide, add a small excess of alkali to a few millilitres of silver nitrate solution, filter out the dark brown precipitate and wash it on the filter with distilled water until the clear filtrate becomes cloudy because of the beginning peptization of the precipitate.

Place 2-3 ml portions of distilled water into three separate test tubes. Add a small quantity of tetramethylammonium iodide into the first, and of tetraethylammonium iodide into the second test tube. Shake both to dissolve the salts. Place pure water into the third test tube and add 2 drops of phenolphthalein into all three test tubes. Using a rod, add small portions of damp silver oxide into all of them.

Shake strongly, add distilled water to fill the test tubes to half their volume, and allow to stand. Note the different colour of the liquids and precipitates.

Amino groups, $-NH_2$, $>NH$, and $\rangle N-$, as well as ammonia NH_3, have a free electron pair at the nitrogen atom. This electron pair can join electrophiles, viz., proton of the acid, and the hydrocarbon radical of alkyl halide, which gives off the electron pair to the halogen and turns into the positive ion of carbonium.

Alkyl halides react with ammonia to give a mixture of products. The first product is a salt of a primary amine:

$$NH_3 + RI \longrightarrow [RNH_3]^+I^-$$

Then in the state of equilibrium with excess of ammonia, a free primary amine is also partly produced:

$$[RNH_3]^+I^- + NH_3 \rightleftharpoons NH_4I + RNH_2$$

It can join the molecule of alkyl halide to form a salt of a secondary amine, $[R_2NH_2]^+I^-$. This gradual alkylation process gives a mixture of salts of the ammonia type, in which one, two, three, or all the four hydrogen atoms in the NH_4^+ ion are replaced by hydrocarbon radicals, viz., $[RNH_3]I$, $[R_2NH_2]I$, $[R_3NH]I$, and $[R_4N]I$.

The ratio of quantities of the formed amine salts depends on the reaction conditions, the character of hydrocarbon radicals and halogens, and on the solubility of the salts.

Amine salts in solution react neutral. As they are heated with alkalis, quite volatile free amines are formed (see Table 8). In aqueous solution, amines react alkaline to litmus, since they form ionizing hydrates with water:

$$(CH_3)_3N + H_2O \rightleftharpoons [(CH_3)_3NH]OH \rightleftharpoons [(CH_3)_3NH]^+ + OH^-$$

The ionization is insignificant and phenolphthalein produces a weak colouration. Amine hydrates are unstable (like ammonium hydroxide, NH_4OH), and when heated, they completely decompose to give free amine.

The ionization constants of the hydrates of lower fatty amines have the values from 5×10^{-4} to 1×10^{-3}, whereas the ionization constant of ammonium hydroxide is only 1.8×10^{-5}. It follows that amines in solution are stronger bases than ammonia (the positive inductive effect of alkyl groups) and ammonium iodide is therefore almost absent in the mixture.

Once the ionization constant (K) of a base and its concentration, in gram-equivalents per litre (C) are known, one can calculate the concentration of hydroxyl ions, i.e. alkalinity of the solution of a base, using the formula $[OH^-] = \sqrt{KC}$ (see also Experiment 75).

Picric acid gives complex compounds with most amines (see also Experiments 163, 241, 242). These compounds well crystallize: the melting points of methylamine and ethylamine picrates are within the range of 150-200 °C. Ammonia and ammonium salts do not form poorly soluble compounds with picric acid, and precipitation of crystals (Experiment 109, D) indicates the presence of amines in solution.

Iodides of tetrasubstituted ammonium are much less soluble than salts of amines. In the described conditions, tetramethylammonium iodide precipitates immediately, while tetraethylammonium iodide precipitates only after removal of part of the solvent. The quaternary salts of ammonium react with alkali or silver oxide to give much stabler hydrates, quaternary ammonium bases, $[R_4N]^+OH^-$, which are strongly (almost completely) ionized in solution and their solutions strongly react alkaline. In the fast ionic reaction (see Experiment 110):

$$2[R_4N]^+I^- + Ag_2O + H_2O \longrightarrow 2AgI + 2[R_4N]^+OH^-$$

the dark brown precipitate Ag_2O turns into yellow AgI, and phenolphthalein produces a bright crimson colouration. Water containing silver oxide is pale pink; this is explained by the partial formation of silver hydroxide, AgOH.

111
Formation of Hydroxamic Acid

REAGENTS

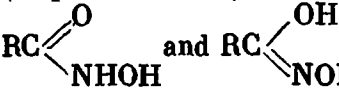
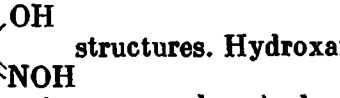
Ethyl acetate (see Experiment 94).
Hydroxylamine hydrochloride, 5 per cent solution.
Ethyl alcohol, rectified.

Place 3-5 drops of ethyl acetate, 0.5 ml of hydroxylamine hydrochloride, 1-2 ml of alcohol, and 3-5 drops of concentrated alkali solution in a test tube. Mix the same reagents (except ethyl acetate) and in the same quantities in another test tube. Heat both tubes to boiling and cool. Add first dilute hydrochloric acid (to acid reaction to litmus) and then 1-2 drops of ferric chloride into each test tube. Note development of colour in one test tube.

Some derivatives of carboxylic acids, namely, esters, anhydrides, acid chlorides, and amides, readily react with hydroxylamine to give hydroxamic acids. If ethyl acetate is added, acet-hydroxamic acid is formed:

$$CH_3COOC_2H_5 + NH_2OH = CH_3CONHOH + C_2H_5OH$$

The same acid is produced if acetic anhydride, acetyl chloride, or acetamide are used instead of ethyl acetate (Experiment 113).

Hydroxamic acids, which are isomeric to aci-nitro compounds (Experiment 108), are soluble in water and can react both as  and  structures. Hydroxamic acids form soluble ferric salts (probably, inner complexes), having the general formula $(RCONHO)_3Fe$; their solutions are bright violet-red (see also Experiments 113 and 195).

112
Preparing Acetamide

REAGENTS

Ammonium acetate, crystalline, or *ammonium carbonate.*

Place 10 g of ammonium acetate, 7 ml of glacial acetic acid into a small round-bottomed flask, and drop a boiling stone. If ammonium acetate is not available, place 15 ml of glacial acetic acid, heat almost to boiling, and slowly add 8 g of ground (in a mortar) ammonium carbonate. Continue heating, shake the flask to obtain a homogeneous mixture, and then drop a boiling stone.

Insert a 25-35 cm long dephlegmator and a thermometer into the flask neck using a cork plug (see Experiment 5). Connect the discharge end of the dephlegmator to a water-cooled condenser. Use a test tube, or a cylinder, having a 10-ml mark, as the receptacle.

Heat the flask on a wire gauze over a burner to vigorous boiling and then adjust the heating so that the distillate drips slowly into the receptacle. The temperature of the vapour should not exceed 105-110 °C. If the entire vapour is condensed in the dephlegmator (before it reaches the thermometer), insulate the dephlegmator with a sheet of asbestos (use only soft wire to tie up the asbestos), and use also asbestos sheets to cover the flask on the sides.

The level of the liquid collected in the receptacle should reach the 10-ml mark in about 60-90 minutes. Continue the distillation until the temperature of the rising vapour is 135-140 °C. Now stop heating, allow the flask to cool slightly, transfer its contents into a test tube with a wide side arm (soldered in its lower part), close the test tube with a stopper through which a thermometer (250 °C) is passed, and distil the product without a condenser. Collect the distillate in calibrated test tubes, cooled in a beaker containing water. A small fraction is collected at temperatures below 190 °C. Change the receptacle and collect the main fraction boiling out within the temperature range of 190-225 °C. The main bulk of this fraction is distilled within a narrow range of temperatures (3-5 °C). The colourless distillate is crystallized on cooling. The yield is 4-4.5 g. The low boiling

fraction also contains a small quantity of acetamide. The obtained product can be used in Experiments 113 and 114.

To purify the acetamide, separate it from oily admixtures on a sheet of filter paper, and wash with a few drops of ether on another sheet of filter paper. Acetamide can also be re-crystallized from benzene. It is very hygroscopic and should therefore be kept in a tightly closed vessel.

Ammonium salts of organic acids decompose on heating as follows:

$$RCOOH + NH_3 \rightleftarrows RCOONH_4 \rightleftarrows RCONH_2 + H_2O$$

Addition of acetic acid shifts the equilibrium in the direction of elimination of water and formation of amide. Water is gradually distilled together with acetic acid. Elimination of water is a slow process and acceleration of distillation therefore strongly decreases the yield of amide.

Ammonium carbonate reacts with acetic acid (taken in excess) according to the equation:

$$(NH_4)_2CO_3 + 2CH_3COOH = 2CH_3COONH_4 + CO_2 + H_2O$$

Ammonium acetate (m.p. 113 °C) reacts with excess acetic acid to form the acid salt $CH_3COONH_4 \cdot CH_3COOH$ (m.p. 66 °C).

Ammonium carbonate gives ammonium acetate with formation of water. Moreover, ammonium carbonate contains a molecule of water of crystallization. Therefore, reaction mixtures with ammonium carbonate contain excess water and require longer distillation (see above); hence the formation of acetamide is retarded.

The specific mousy odour of the acetamide preparation is accounted for by the presence of a small quantity of impurities that are difficult to separate.

113
Reactions of Acetamide

REAGENTS

Acetamide, (see Experiment 112).
Mercuric oxide, yellow powder.
Hydroxylamine hydrochloride, 5 per cent solution.

Prepare a solution of 0.5-1 g of acetamide in 5-7 ml of water. Test it with litmus and use for the following reactions.

A. Alkalize part of the solution with sodium hydroxide and boil: a pungent specific odour can be felt.

B. Acidify another portion of the solution with dilute sulphuric acid and boil: a specific odour, other than in A, is felt.

C. Add a small quantity of mercuric oxide to a portion of the solution and shake to dissolve it. Add a small quantity of dilute sodium hydroxide solution until the mixture strongly reacts alkaline and heat until a white precipitate falls out and the pungent odour is felt.

D. Add 1 ml of hydroxylamine hydrochloride to a portion of the solution. Transfer half of the obtained mixture into another test tube, boil for 2-3 minutes, and cool. Add a few drops of ferric chloride solution to both test tubes: intense red colouration develops in one of them.

Acetamide very readily dissolves in water, worse in ethyl alcohol, and does not dissolve in ethyl ether. Aqueous solution of acetamide reacts neutral, but the hydrogen atoms in the NH_2 group can be replaced by metals. For example, acetamide easily reacts with mercuric oxide to give a readily soluble mercury compound $(CH_3CONH)_2Hg$. Alkali fails to precipitate mercuric oxide from its solution and this indicates that the character of bond of mercury in this compound is not ionogenic. When the solution is heated with alkali, it is hydrolysed, but one nitrogen atom remains bonded with mercury, and a mercury-amide compound (acetate in our case), which is insoluble in water or alkali, is formed:

$$(CH_3CONH)_2Hg + NaOH + H_2O \longrightarrow CH_3COONa + NH_3 + [NH_2Hg]^+CH_3COO^-$$

Hydrolysis of free amides of acids, on boiling with alkalis or mineral acids,

$$RCONH_2 + H_2O \longrightarrow RCOOH + NH_3$$

occurs quite rapidly and is accelerated not only by the catalytic action of the OH^- and H^+ ions, but also by bonding organic acid in the former, and ammonia in the latter case.

The amides of fatty acids are characterized by easiness with which the NHOH group is substituted for the NH_2 group. The substitution takes place during boiling with solutions of hydroxylamine salts:

$$RCONH_2 + NH_2OH \longrightarrow NH_3 + RCONHOH$$

Hydroxamic acids that are formed in this reaction can easily be detected since they react with an ion of tervalent iron to give intensely coloured complex salts (cf. also Experiments 111 and 195).

114
Formation of Methylamine from Acetamide and Its Properties

REAGENTS

Acetamide (see Experiment 112).
Bromine.
Ethyl alcohol.
Chloroform.

Place 1 g of acetamide, 3-5 ml of water, and 1 ml of bromine into a 75-100 ml flask provided with an outlet tube. Shake the mixture and cool the flask in water. Slowly add concentrated alkali solution until the bromine colour vanishes. Add about the same volume of the alkali in excess. In 10-15 minutes, drop a boiling stone, connect a condenser to the outlet tube, and distil methylamine into a receptacle containing 1-2 ml of water and cooled to 0 °C. The end of the condenser, or of a special adaptor (see Fig. 2*d*) should be immersed in water. Discontinue the distillation when the liquid volume in the receptacle increases 3-4 times.

The distillate has the specific odour of methylamine.

A. Add a drop of methyl orange to a portion of the distillate and then add, drop by drop, dilute hydrochloric acid until the solution reacts acid. A considerable quantity of the acid is required.

B. Add an equal volume of alcohol to 1-2 ml of methylamine, then add 2 drops of chloroform and 1 ml of concentrated alkali solution. The experiment should be carried out in the HOOD. As the mixture is heated, the specific and unpleasant odour of isonitrile is felt. At the end of the experiment, immerse the test tube in a bath containing dilute sulphuric acid, or hydrochloric acid, to decompose isonitrile.

C. Add methylamine, drop by drop, to 0.5-1 ml of copper sulphate solution: blue copper hydroxide first precipitates, and then dissolves to colour the solution intense blue.

The solution of methylamine can be used in Experiment 252.

Bromine reacts with alkali to give a hypobromite:

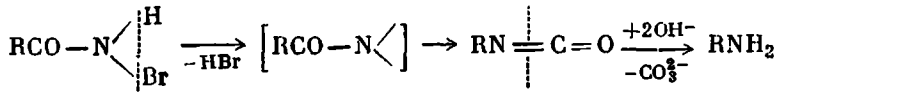
$$Br_2 + 2NaOH \longrightarrow H_2O + NaBr + NaOBr$$

The hypobromite reacts with acid amides to replace one of the amide hydrogens by bromine:

$$RCONH_2 + NaOBr \longrightarrow NaOH + RCONHBr$$

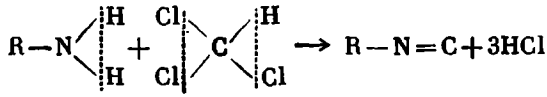
Alkali eliminates hydrogen bromide from the bromamide. The remainder of the molecule is re-grouped into the ester of isocyanic

acid, which (in the conditions of the experiment) is split by aqueous alkali to give a carbonate and a free primary amine:



In this process, known as the Hofmann conversion of amides, one carbon atom is removed from the molecule, and the amino group is substituted for the carboxyl group COOH (through $CONH_2$). This reaction is therefore often used to establish the structure of newly synthesized or natural organic substances.

The properties of fatty amines were discussed above (Experiments 109 and 110). Only a primary amine is formed in this reaction. The reaction in which isonitrile is formed (Experiment B) by the action of alkali and chloroform is characteristic of primary amines (cf. Experiment 209). The chemistry is as follows:



The intermediate product in this reaction is presumably also dichlorocarbene, $>CCl_2$ (cf. Experiment 35).

The odour of isonitriles is very unpleasant. Isonitriles are unstable and resinified on storage. They are rapidly hydrolysed by acids to give the salt of the original amine and formic acid:

$$R-N{\equiv}C+HCl+2H_2O \longrightarrow [RNH_3]^+Cl^- + HCOOH$$

Being a relatively strong base, methylamine precipitates copper hydroxide from solutions of salts of divalent copper. But excess amine reacts with copper ions to form complex compounds readily soluble in water (Experiment C). These compounds contain the complex ion $[Cu(CH_3NH_2)_4]^{2+}$ and are similar to copper ammoniates. Their solutions are also intense violet.

115
Formation of Ethylamine from Acetamide

REAGENTS

Acetamide (see Experiment 112).
Sodium metal.
Ethyl alcohol, rectified.

Dissolve 0.5-1 g of acetamide in 6-7 ml of alcohol in a test tube. Add 2-3 grains of sodium metal (dried in filter paper) and close quickly the test tube with a stopper through which an outlet tube is passed. Lower the end of the tube almost to the bottom of a recepta-

cle containing 2-3 ml of alcohol. Hold both test tubes in the hands and shake the former at times. The reaction is vigorous. When the sodium grains are completely dissolved, fix the former test tube in the stand. The volatile reaction products, delivered into the receptacle together with hydrogen, have specific odour. Use the liquid collected in the receptacle in Experiments A, B and C, as instructed in the previous experiment.

Metallic sodium reacts with alcohol to liberate hydrogen (cf. Experiment 40), which at the moment of its liberation reduces an acid amide to a primary amine having the same number of carbon atoms:

$$RCONH_2 + 4H = RCH_2NH_2 + H_2O$$

(see the previous experiment). The chemical properties of ethylamine and methylamine are absolutely the same.

116
Formation of Salts of Urea with Acids

REAGENTS

Urea.
Oxalic acid, powder.

Dissolve 1 g of urea in 5 ml of water. Use the solution in this experiment, and also in Experiments 117 and 118.

A. Place 1 ml of urea solution in a test tube and carefully add 1 ml of concentrated nitric acid: a white ring of crystals forms at the interface of the two liquid layers. Shake the mixture and cool: ample crystalline precipitate falls out.

B. Prepare a saturated at room temperature solution of oxalic acid (0.1-0.2 g of the acid per 1-2 ml of water). Mix 1 ml of this solution with an equal volume of urea: crystals precipitate in a few seconds.

Urea, $CO(NH_2)_2$, is a full amide of carbonic acid. It is readily soluble in water. In aqueous solution it has two tautomeric forms:

$$H_2N-\underset{\underset{O}{\|}}{C}-NH_2 \rightleftharpoons H_2N-\underset{\underset{OH}{|}}{C}=NH$$

Urea solution reacts neutral to litmus. But it reacts with acids in the cold to give salts of urea with one equivalent weight of acid. The nitrate, $CO(NH_2)_2 \cdot HNO_3$, and oxalate, $[CO(NH_2)_2]_2 \cdot H_2C_2O_4$, sparingly dissolve in water and readily crystallize.

Urea undergoes hydrolysis in an acid medium with heating (cf. Experiments 113 and 118).

117
Reactions of Urea with Liberation of Nitrogen

REAGENTS

Urea, 15-20 per cent solution (see Experiment 116).
Potassium (sodium) nitrite, 10 per cent solution.
Sodium hypobromite, prepared before for the experiment.

Prepare sodium hypobromite solution as follows. Add 3-4 drops of bromine to 1-2 ml of concentrated solution of sodium hydroxide and shake the mixture to dissolve bromine (until the colour of bromine vanishes).

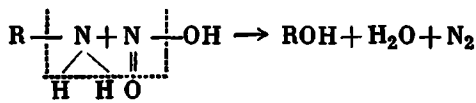
A. Place 1 ml of urea solution in a test tube and add 0.5 ml of the nitrite solution. Then add dilute sulphuric acid, drop by drop, with shaking and cooling: gas is liberated in ample quantities. Unlike nitrogen oxides, which are the products of decomposition of nitrous acid, the liberated gas has no pungent odour, nor is it brown.

B. Place 1 ml of urea solution in a test tube and add, drop by drop, sodium hypobromite: a colourless and odourless gas is liberated in ample quantities. Ammonia is not formed in the conditions of the experiment. Formation of ammonia is characteristic of urea reaction with alkali (cf. Experiment 118).

In an acid medium nitrites give nitrous acid that decomposes to liberate nitrogen oxides

$$2HNO_2 \longrightarrow NO + NO_2 + H_2O$$

Compounds containing amino group quickly react with free nitrous acid (cf. Experiment 210). If primary fatty amines, amides of acids, or ammonia are added, nitrogen is liberated as a result of substitution of hydroxyl for the amino group:



The intermediate products are as a rule less stable in this case than aromatic diazo compounds (cf. Experiment 211). Primary amines are converted by this method into alcohols, and amides of acids into free acids. Urea (Experiment A) converts into carbonic acid, which is liberated as anhydride:

$$CO(NH_2)_2 + 2HNO_2 \longrightarrow 3H_2O + CO_2 + 2N_2$$

This reaction is often used to remove nitrous acid from solution.

The action of bromine and alkali on acid amides is very complicate (see Experiment 114). The summary reaction equation is as follows:

$$RCO-NH_2+NaOBr+2NaOH \longrightarrow RNH_2+Na_2CO_3+NaBr+H_2O$$

In conditions of Experiment B, urea reacts first to give hydrazine, NH_2-NH_2, which is then oxidized with excess hypobromite to liberate nitrogen:

$$NH_2NH_2+2NaOBr \longrightarrow 2NaBr+2H_2O+N_2$$

Nitrogen is liberated smoothly and quickly. The method is used for quantitative determination of urea (A. P. Borodin, 1875).

118
Hydrolysis of Urea with Heating

REAGENTS

Urea.

Barium hydroxide, saturated solution.

A. Place 1 ml of urea solution (see Experiment 116) in a test tube and add 2 ml of clear baryta water. Heat the mixture: two reaction products are formed, namely gas, which is detected by the odour and by litmus paper (turns blue), and barium carbonate, which precipitates.

B. Place 0.2-0.3 g of urea in a dry test tube and heat over a burner. Urea first melts, and then ammonia is vigorously liberated. The melt gradually thickens and then hardens again despite the continuing heating. A white coat is deposited on the cold parts of the test tube. Cool the test tube, add 1-2 ml of warm water, shake, and transfer the liquid into another test tube. Add 3-4 drops of alkali to the obtained cloudy solution of biuret until it becomes clear, and a drop of copper sulphate solution: the specific colour develops.

Extract the solid residue in the former test tube with warm water and add 2-3 ml of water to the extract. Boil the mixture for a few minutes. Cool and add a few drops of copper sulphate solution and 1 ml of ammonia solution: a violet precipitate falls out.

Hydrolysis of acid amides was discussed in Experiment 113.

When urea is heated to a temperature exceeding its melting point, it decomposes with liberation of ammonia. At 150-160 °C two molecules of urea eliminate one molecule of ammonia to give biuret, which is well soluble in warm water:

$$H_2N-CO-NH_2+H-NH-CO-NH_2 \longrightarrow H_2N-CO-NH-CO-NH_2+NH_3$$

Biuret reacts with copper salts in an alkaline medium to give a bright red complex compound, having the following composition (in KOH solution):

$(NH_2CONHCONH_2)_2 \cdot 2KOH \cdot Cu(OH)_2$

A similar 'biuret reaction' (development of red, blue, or violet colouration of alkaline solution in the presence of copper salts) is characteristic of many compounds containing several —CONH— groups (reacting in the tautomeric form —C(OH)=N—), e.g. proteins and products of their decomposition (Experiment 282).

If urea is rapidly and strongly heated, the ammonia molecule is eliminated from each molecule of urea (not from two molecules as in the previous case) to give cyanic acid, HNCO, which readily turns into cyclic trimeric cyanuric acid $(HCNO)_3$. Cyanuric acid is formed (with elimination of ammonia) by heating biuret as well. The acid is tribasic, it forms stable salts, sparingly dissolves in water, and partly decomposes on heating to give cyanic acid again.

The sublimate on the walls of the test tube is the monomeric ammonium cyanate, NH_4OCN. The violet precipitate is the complex cuprammonium salt of cyanuric acid, $Cu(C_3H_2N_3O_3)_2 \cdot 2NH_3$.

119
Reactions of Glycine

REAGENTS

Glycine.
Formalin.
Cupric carbonate, powder.
pH test paper.
Sodium hydroxide, dilute solution stained with phenolphthalein; prepare the alkali solution immediately before the experiment.

A. Determine the acidity (pH) of an aqueous solution of glycine using test paper.

B. Place 2-3 ml of glycine solution in a test tube and add the stained alkali solution, drop by drop, until a persistent colour develops (which is attained at once). Place 1 ml of formalin and 3-4 ml of water into another test tube and also add alkali until the colour develops. Mix both coloured solutions and observe discolouration of the mixture, i.e. development of acid reaction as a result of mixing two alkaline solutions. As the coloured alkali solution is further gradually added, the phenolphhalein colour continues to vanish.

C. Place 1-ml portions of copper sulphate solution into two separate test tubes, and add 1 ml of glycine to one of them. Note the different colours of the solutions. Now add 1 ml of dilute alkali into both

test tubes (without indicator) and observe precipitation of copper hydroxide in one of them.

D. Place a small quantity of cupric carbonate powder into a test tube, add 4-5 ml of glycine solution and heat the mixture. The liquid foams and turns bright blue. Allow the hot mixture to settle, decant the greater portion of the clear liquid into another test tube, and allow it to cool: blue crystals precipitate.

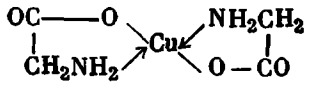
Glycine (glycocoll, α-aminoacetic acid) is a constituent part of many proteins (see Chapter 21). The presence of the amino group in its molecule strongly weakens the acid properties of glycine (cf. Experiment 75). For glycine, K_1 is 1×10^{-10}, and its aqueous solution only slightly reacts acid (Experiment A). Free glycine has the structure of the 'inner salt' and in solution it forms the dipolar ion $^+NH_3CH_2COO^-$ (cf. Experiment 206).

The amino group in the glycine molecule can be either replaced, e.g. by hydroxyl group (by the action of nitrous acid; cf. Experiments 117 and 211), or bonded by different ways. For example, like other amino acids, glycine quickly reacts with formaldehyde in an aqueous solution:

$$H_2CO + NH_2CH_2COOH \longrightarrow H_2O + H_2C{=}NCH_2COOH$$

Methyl derivatives with the groups $-NHCH_2OH$ and $-N(CH_2OH)_2$, can also be formed simultaneously (cf. Experiment 268). Unlike glycine, its derivatives, formed in these reactions, have strongly acid properties (Experiment B). Amino acids are therefore easily titrated with alkali, provided formaldehyde is added (the formol titration).

The copper salt of glycine forms a stable inner complex compound. Its blue colour is characteristic of divalent copper complexes (cf. Experiments 51, 90, 125):



This complex salt of glycine is sparingly soluble in cold water (Experiment D). In Experiment C, glycine reacts with copper sulphate to give this salt and free sulphuric acid. The experiment shows that the inner complex salt is stable in acid and alkali media.

Glycine reacts with cupric carbonate, $Cu_2(OH)_2CO_3$ (Experiment D), to clearly reveal its acid properties. The liberation of CO_2 is explained by that the amino group of its molecule is bonded in the complex. For the same reason, even copper oxide boils with glycine solution to pass partly into solution and to colour it blue.

CHAPTER ELEVEN

CARBOHYDRATES

Glucose and fructose are used as monosaccharides in many experiments. If pure sugars are not available, potato starch syrup, or starch sugar can be used instead of glucose, and honey containing glucose and fructose (approximately in equal quantities) instead of fructose. Invert sugar, obtained by hydrolysis of ordinary beet or cane sugar (saccharose), is also a mixture of glucose and fructose, and gives characteristic reactions of the latter. Fructose solution is also formed by boiling crushed *dahlia* tubers, or Jerusalem artichoke tubers with dilute hydrochloric acid.

The most available disaccharide is saccharose, but disaccharides of other structures should also be used, e.g. reducing sugars, maltose and lactose.

Lactose can be prepared from milk. Act as follows. Precipitate casein (see Chapter 21), pass the whey through a filter, boil the filtrate, cool, separate the coagulated proteins by filtration, neutralize the liquid with dry magnesium carbonate, and evaporate to dryness on a water bath. Mix the residue with 5 ml of alcohol, decant the liquid, dissolve the crystals in 10 ml of water, filter, evaporate to 3 ml and add 4 ml of alcohol. Crystals of lactose precipitate on standing. The yield is 1.5-1.8 g.

Milk whey, from which proteins are removed, can be used instead of crystalline lactose in Experiments 125, 126 and 136.

Starch and cellulose (filter paper or cotton wool) should be used as polysaccharides in experiments.

All carbohydrates are solid, often crystalline substances. Most mono- and disaccharides are readily soluble in water and are often precipitated from solution as crystal hydrates. When heated carbohydrates decompose without sublimation. Some carbohydrates have characteristic melting points (see Table 9), but some sugars are characterized by the melting points of their various derivatives.

Table 9

Melting Points of Sugars

Substance	Formula	M. p., °C
D-Glucose	$C_6H_{12}O_6$	146
Glucose hydrate	$C_6H_{12}O_6 \cdot H_2O$	82
D-Fructose	$C_6H_{12}O_6$	95
D-Galactose	$C_6H_{12}O_6$	166
Galactose hydrate	$C_6H_{12}O_6 \cdot H_2O$	119
D-Mannose	$C_6H_{12}O_6$	132
Saccharose	$C_{12}H_{22}O_{11}$	160
Maltose (hydrate)	$C_{12}H_{22}O_{11} \cdot H_2O$	100 (decomp. at 110)
Lactose (hydrate)	$C_{12}H_{22}O_{11} \cdot H_2O$	203 (with decomp.)

In order to preclude erroneous and dubious results, it is necessary to take measures against contamination of one sugar with another in the process of preparation to the experiments and in the course of the procedure.

For obtaining furfural from pentoses see Chapter 17. For reactions of lignin see Chapter 14.

Lactose and fructose were first obtained and studied at St. Petersburg Academy of Sciences late in the 18th century. N. P. Sokolov carried out his investigations with lactose and T. E. Lovits with fructose.

120
General Reaction for Carbohydrates with α-Naphthol (Molisch's Test)

REAGENTS

Carbohydrates, e.g. sugars, starch, cellulose.

α-Naphthol, 10 per cent solution in alcohol or chloroform. The solution should preferably be prepared immediately before the experiment.

Carry out parallel tests with several different carbohydrates.

Place 0.5-1 ml of water in a test tube and add a very small quantity of a carbohydrate, e.g. a few grains of sugar, or starch, or a small piece of filter paper, sizing 2-3 mm². Add 2 drops of α-naphthol solution. If an alcoholic solution of α-naphthol is used, the mixture becomes slightly cloudy because naphthol is sparingly soluble in water. Incline the test tube and carefully add, better from a pipette, 1-1.5 ml of concentrated sulphuric acid. The heavy acid lowers to the bottom almost without mixing with the aqueous layer. A red-violet

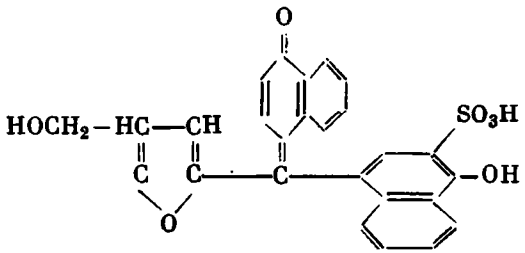
ring forms at the interface of the layers. If the mixture is shaken, it gets hot and coloured throughout its entire volume. Add water: coloured flakes precipitate.

The violet ring is not formed in the absence of carbohydrates, although the liquid can turn green or yellow.

Carbohydrates give the coloured reaction with α-naphthol (Molisch's test, 1886). Ketoses (free or bonded in disaccharides and polysaccharides) react more intensely. The colouration is accounted for by splitting of the carbohydrate molecule by the concentrated sulphuric acid, with formation of furfural or its derivatives (among other reaction products) that take part in the condensation reaction with α-naphthol to give coloured compounds. Other compounds, capable of condensation with furfural derivatives into coloured products, can be used instead of α-naphthol. Resorcinol produces orange-red colouration in these conditions (cf. Experiment 133), thymol gives red colour, and diphenylamine, blue.

In the presence of salts of nitrous, nitric, hydrobromic, and hydriodic acids this qualitative test is insufficiently reliable.

The coloured product formed in the described conditions from hexose and α-naphthol has the following structure:



The colour test for carbohydrates described above is very sensitive. Even minute fibres of filter paper or dust, which can incidentally get into the test tube, can produce the positive reaction with α-naphthol. Some compounds, other than carbohydrates, e.g. tannin, which contains the glucose residue in its molecule, and also pyrogallol, can give this reaction as well. If the solution contains pyrogallol, dilution with water removes the colouration.

Some proteins (glucoproteins) contain carbohydrates bonded with peptides and give the specific reaction with the Molisch reagent. Egg albumin and saliva mucin are examples of such proteins.

Colour reactions with formation of a coloured ring at the interface of the liquid layers are often very convenient (cf. Chapter 21). This

method is relatively more sensitive, since the diffusion at the interface accounts for the different ratios of concentrations of the reactants at various levels, including the ratio at which the appearance of distinct colouration becomes more favourable.

121
Reaction of Carbohydrates with Concentrated Acids

REAGENTS

Any *sugar* (*glucose* and *fructose* included).

A. Dissolve a few grains of sugar in a test tube in 1-2 ml of water. Carefully add an equal volume of concentrated sulphuric acid, pouring it on the wall and trying not to stir the mixture. Sulphuric acid lowers to the bottom, to underlie the sugar layer. A dark brown ring is formed at the interface. If otherwise, gently heat without jolting.

B. Place a small quantity of glucose into a test tube, add 2 ml of concentrated hydrochloric acid, and boil for 20-30 seconds. Cool the solution and add water to fill the test tube to 2/3 its capacity. Repeat the experiment using fructose instead of glucose. Note the distinct difference in the appearances of the two solutions.

Concentrated mineral acids split carbohydrates into a mixture of various products: furfural and its derivatives, levulinic and formic acids, and humins. The complicate structure of humins has not yet been established. They are dark brown or black, sparingly soluble substances that are isolated in the experiment at the interface. Ketoses are split by acids faster than aldoses. The test B can be used for quick differentiation of fructose from glucose.

122
Formation of Sugar by Oxidation of Polyhydric Alcohol

REAGENTS

Glycerol (see Chapter 6).
Mannitol (see Chapter 6).
Bromine water (saturated, prepared immediately before the experiment).

Carry out the tests with glycerol and mannitol simultaneously.

Place 3-4 drops of glycerol and 0.1-0.2 g of mannitol into separate test tubes. Dissolve the substances in 3 ml of water, and divide each solution into two halves. Add equal volumes of dilute alkali and 2-3 drops of copper sulphate solution to the first portions of the solu-

tions: blue copper hydroxide precipitates, but it dissolves on shaking to colour the solution violet or blue. Heat the solution to boiling and observe the changes if any.

Add 8-10 ml of saturated bromine water to the remaining halves of glycerol and mannitol solutions and heat on a boiling water bath until they are decolourized. If the colour does not disappear in 10-15 minutes, boil the solutions for 1-2 minutes over a burner. Cool the colourless liquid, transfer 2-3 ml into test tubes, add alkali and copper sulphate as instructed above, and heat to boiling.

Polyhydric alcohols, e.g. glycerol, $CH_2(OH)CH(OH)CH_2OH$, or mannitol, $CH_2OH(CHOH)_4CH_2OH$, having several hydroxyl groups in their molecules, can dissolve copper hydroxide (cf. Experiment 51). The first test of this experiment shows that divalent copper in alkaline solution is insufficiently strong oxidant to oxidize these alcohols. Bromine water is a more energetical oxidant and it converts a polyhydric alcohol mainly into hydroxyaldehyde, aldose:

$$Br_2 + H_2O \rightleftarrows HBr + HOBr$$

$$CH_2OH(CHOH)_nCH_2OH + HOBr \longrightarrow CH_2OH(CHOH)_nC\begin{matrix}=O\\ \diagdown H\end{matrix} + HBr + H_2O$$

Hydroxyketone, ketose, is formed simultaneously. If bromine water is taken in excess, aldose is partly oxidized to oxyacid (cf. Experiment 129).

Glycerol is oxidized with bromine water to give a mixture of trioses, viz., glycerose (glyceric aldehyde, $CH_2(OH)CH(OH)CHO$, and dihydroxyacetone, $CH_2(OH)COCH_2OH$). Mannitol is oxidized with bromine water to give hexoses (mannose and fructose). All these compounds are monosaccharides and give characteristic reactions. For example, unlike the original alcohols, they are readily oxidized by divalent copper in alkaline solution to give the corresponding oxyacids with precipitation of copper or cuprous oxide (Trommer test, see Experiments 59 and 125).

123
Formation of Glucose Osazone

REAGENTS

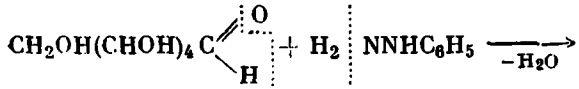
Glucose.
Phenylhydrazine hydrochloride, pure, crystalline, almost colourless.
Sodium acetate, crystalline.

Mix two parts by weight of phenylhydrazine hydrochloride with three parts by weight of sodium acetate, and thoroughly grind tn a mortar.

Dissolve about 0.2 g of glucose in 4 ml of distilled water, add about 1 g of the prepared mixture of salts, and heat on a boiling water bath for 5-10 minutes with shaking at short intervals. When yellow crystals of osazone appear, place the test tube in the stand and allow it to cool slowly. Beautiful yellow needles of glucose osazone gradually crystallize.

Phenylhydrazine acetate is formed by the exchange reaction that occurs in the solution of the mixture of phenylhydrazine hydrochloride and sodium acetate. Being a salt of a weak acid and a weak base, phenylhydrazine acetate is strongly hydrolysed and is equilibrated in solution with free phenylhydrazine, $C_6H_5NHNH_2$, which reacts with sugar. Direct use of free phenylhydrazine is less convenient, since it is sparingly soluble in water; moreover, it is harmful for man.

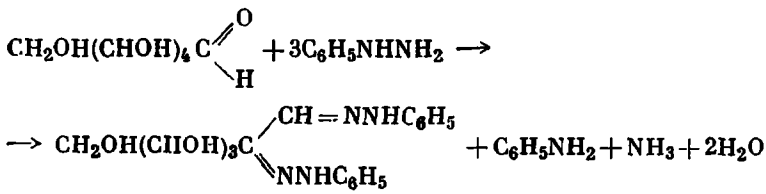
Phenylhydrazine reacts with carbonyl groups of aldehydes, ketones, and sugars to give phenylhydrazones (cf. Experiment 179). It reacts with glucose according to the equation:



$$\longrightarrow CH_2OH(CHOH)_4CH=NNHC_6H_5$$

Phenylhydrazones of many sugars are well soluble in water. Less readily soluble are phenylhydrazones of galactose, arabinose, and especially of mannose.

In the presence of excess phenylhydrazine, one molecule of glucose reacts with two more molecules of phenylhydrazine. Intramolecular conversions of unstable intermediate compounds give ammonia, aniline, and osazone of the original sugar (which contains two adjacent phenylhydrazine groups). The summary equation of the reaction in which glucose osazone is produced is as follows:



These processes have been studied in detail by the Russian academician M. M. Shemyakin.

Sugar osazones are commonly less soluble in water than phenylhydrazones. The shape of their crystals is quite specific (microscopy) and osazones are therefore often used for identification of sugars. The melting points of many osazones are not very characteristic and vary depending on the rate of heating. The study of osazones is espe-

cially important in determining steric isomerism of sugars. Thus, in accordance with the steric structure of glucose, fructose, and mannose, these sugars form the same osazone.

In conditions of the given experiment, even in the presence of excess phenylhydrazine, mannose gives crystals of sparingly soluble phenylhydrazone that quickly precipitate from solution. Osazones of other sugars precipitate at various speeds, depending on the easiness of their formation and solubility: osazone of fructose is the fastest to precipitate from a hot solution. Osazones of glucose, xylose, and arabinose precipitate slower. Galactose osazone has the slowest precipitation rate. Osazones of lactose and maltose are relatively better soluble in hot water, and they precipitate only on cooling. The melting point of glucose osazone is 209 °C (with decomposition).

The hydrolysis of phenylhydrazone of sugar gives the original sugar, and the hydrolysis of osazone gives the product of oxidation of sugar, containing two carbonyl groups, osone.

The molecule of saccharose has neither free carbonyl groups, nor glucoside hydroxyls that could form the carbonyl group through tautomerization. Saccharose therefore reacts with phenylhydrazine only very slowly to give glucosazone by gradual hydrolysis.

124
Reaction of Sugars with Alkalis

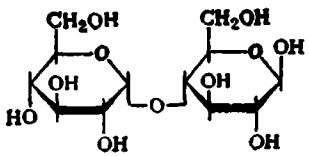
REAGENTS

Monosaccharides, e.g. *glucose*, *galactose*, *fructose*.
Disaccharides, e.g. *saccharose*, *lactose*, *maltose*.

Carry out simultaneously several tests with various sugars, using their 5-10 per cent solutions, or solutions obtained by dissolving 0.1-0.2 g of sugar in 1-2 ml of water.

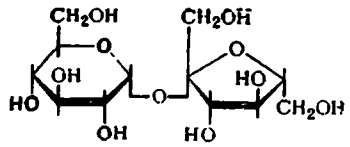
Place 1-2 ml of sugar solution into a test tube and add half volume of concentrated alkali solution. Boil the mixture for 2-3 minutes: note the colour change, if any. Cool the liquid and acidify with dilute sulphuric acid: the colour intensity diminishes and the odour of caramel (burnt sugar) is felt.

All sugars that have a free glucoside hydroxyl in the oxide form and a free carbonyl group in the open form, i.e. all monosaccharides and some disaccharides, e.g. maltose:



are easily resinified by heating in an alkaline solution (like aldehydes or ketones; cf. Experiment 63) to give a brown or black solution.

Resinification gives a complex mixture of substances. Sugar is partly isomerized in different directions, and partly is decomposed to give lactic acid and other compounds. Sugar and its products are simultaneously oxidized by atmospheric oxygen (cf. Experiment 132) and by the dehydration process (Experiment 131). The products of sugar resinification contain several free hydroxyl groups and, unlike aldehyde resin (see Experiment 63), therefore readily dissolve in water, and especially in alkalis. In the molecule of saccharose



(sucrose) residues of glucose and fructose are bonded by two glucoside hydroxyls. Isomerization with formation of a carbonyl group therefore becomes unfeasible, and the action of alkalis on saccharose solution does not produce resinification. Lengthy boiling of such a mixture causes gradual hydrolysis of saccharose. The formed monosaccharides are resinified.

Very weak alkalis do not produce such deep changes in sugars: nevertheless, sugars are still capable of isomerization. For example, glucose partly converts into mannose and fructose in these conditions.

Cyclic (oxidic) formulas for sugars were first proposed by the Russian scientist A. A. Kolli (1870). He was the first to synthesize disaccharides in 1879.

125
Reaction of Sugars with Cupric Salts in Alkaline Solution

REAGENTS

Monosaccharides, e.g. *glucose*, *galactose*, *fructose*.
Disaccharides, e.g. *saccharose*, *maltose*, *lactose*.

Carry out simultaneously several tests with different sugars. Dissolve 0.05-0.1 g of each sugar in 2-3 ml of water.

Place 2-3 ml of sugar solution into a test tube and add 1 ml of dilute alkali solution and 2-3 drops of copper sulphate: copper hydroxide precipitates. Shake the mixture: the precipitate dissolves and the liquid colours intense blue. Carefully heat the upper portion of the liquid over a burner until it starts boiling. If sugar is oxidized,

the blue colour of the solution changes to green, and then disappears. Yellow, red, or brown precipitate falls out.

The formation of easily soluble, intensely coloured, and stable to alkali complex alcoholates of copper by the reaction between solutions of sugars and cupric hydroxide proves the presence of several adjacent hydroxyl groups in the sugar molecule (cf. Experiments 51 and 90).

A. A. Kolli was the first to establish the presence of five hydroxyl groups in the molecule of hexose (glucose) (1869).

When heated in an alkaline solution, sugars reduce divalent copper that is present in solution, and are oxidized to give a complicate mixture of water-soluble substances, mostly oxyacids. The resultant products are bright coloured insoluble substances (cuprous hydroxide, CuOH, cuprous oxide, Cu_2O, and metallic copper) (cf. Experiment 59).

Compounds of divalent copper can be reduced in an alkaline solution with heating only by sugars that have a free glucoside hydroxyl in their molecule, or, which is actually the same, a free carbonyl group, i.e. by monosaccharides, and most disaccharides and trisaccharides.

The reaction described above (Trommer's test) is often used to detect such *reducing sugars* in solution.

In accordance with its structure, saccharose does not show reducing properties in these conditions and begins to oxidize with precipitation of yellow cuprous hydroxide only after a long boiling. This is explained by the formation of monosaccharides in the hydrolysis.

126
Reaction of Sugars with Fehling's Solution

REAGENTS

Glucose, *fructose*, *galactose*, *saccharose* (1-2 per cent solution).

Solution A: *copper sulphate* (3.5 g of $CuSO_4 \cdot 5H_2O$ in 50 ml of water).

Solution B: *sodium-potassium tartrate* in water-alkali solution (17.3 g of Seignette's salt and 6 g of sodium hydroxide in 50 ml).

Carry out simultaneously several tests with different sugars.

Accurately measure out and mix equal volumes of solutions A and B, and place 2-ml portions of the obtained dark blue liquid into test tubes. The number of the test tubes should correspond to the number of sugars under study. Heat each test tube until the liquid begins boiling and add, drop by drop, 0.5-1.5 ml of the test solution of sugar (seeing to it that the boiling does not stop) until the blue colour

of the solution completely vanishes and red cuprous oxide precipitates. If a sugar solution is added from a graduated pipette or a burette, the concentration of the sugar solution can be estimated in many cases.

The reduction of divalent copper to monovalent by reducing sugars (see the previous experiment) is more smooth if copper hydroxide is dissolved in the alkaline medium before sugar is added. Sodium-potassium tartrate, $C_4H_4O_6NaK \cdot 4H_2O$, is used for the purpose in Fehling's solution (see Experiment 90).

The concentrations of solutions A and B are so selected that the blue colour is removed by adding 10 mg of monosaccharide (glucose, fructose, galactose, etc.) to 2 ml of their mixture.

In our experiment, disaccharides are hydrolysed to monosaccharides only insignificantly, therefore to discolour 2 ml of Fehling's solution, 14-18 mg of reducing disaccharides, e.g. maltose or lactose, are required. Saccharose almost does not react in these conditions.

For accurate determination of sugars with Fehling's solution, the quantity of the formed cuprous oxide is assessed gravimetrically or titrimetrically, and sugar content calculated using special tables (compiled from experimental data).

Sometimes, the tartrate is replaced by citrate, and soda is used instead of caustic alkali in Fehling's solution. This Benedict's modification of Fehling's solution contains the copper-citrate complex. Glycerol can be used instead of salts of oxyacids (see Experiment 51).

A mixture of copper acetate and acetic acid can also be used. The mixture oxidizes sugars on heating in an acid medium, but the process is less energetic than with Fehling's solution. This acid reagent, known as Barfoed's solution, therefore reacts not with all reducing sugars. For example, it does not react with disaccharides maltose and lactose.

127
Reaction of Sugars with Ammoniacal Silver Oxide Solution

REAGENTS

Any *sugar* (*monosaccharide* or *disaccharide*, except saccharose), 1-2 per cent solution.

Ammoniacal *silver oxide* solution (prepared immediately before the experiment).

Prepare the solution as follows. Add, drop by drop, ammonia solution in water to 1-2 per cent silver nitrate solution until the precipitate, which first falls out, is all dissolved. Add 1/10 volume of dilute sodium hydroxide solution to the obtained liquid. Do not prepare

the reagent in quantities larger than required for the experiment and do not keep it for a long time (see Experiment 60).

Thoroughly wash a test tube with alkali solution and rinse with water. Place 1 ml of ammoniacal silver oxide solution into the test tube and add 1 ml of sugar solution. Mix the contents and place the test tube in a hot bath (60-80 °C). If the test tube is perfectly clean, a silver mirror is deposited on the walls (sugar is oxidized to reduce silver). If the test tube is not clean, a black substance precipitates.

This reaction was discussed in detail in Experiment 60. Reducing sugars, both aldoses and ketoses, are readily oxidized by silver oxide in an alkaline solution. Saccharose is oxidized by this reagent only after inversion (see Experiment 135). Reduction of silver with sugars is utilized in the manufacture of mirrors.

Aldose solution contains mainly cyclic (oxide) forms of aldoses, whereas aldehyde forms, containing a free aldehyde group, are present only in small quantities. These solutions, therefore, give the reaction for aldehyde group with Schiff's reagent only on the condition that the reagent does not contain excess sulphur dioxide (see Experiment 61) and the aldose concentration is high; the reaction is very slow even with a highly sensitive reagent.

128
Formation of Levulinic Acid from Hexoses

REAGENTS

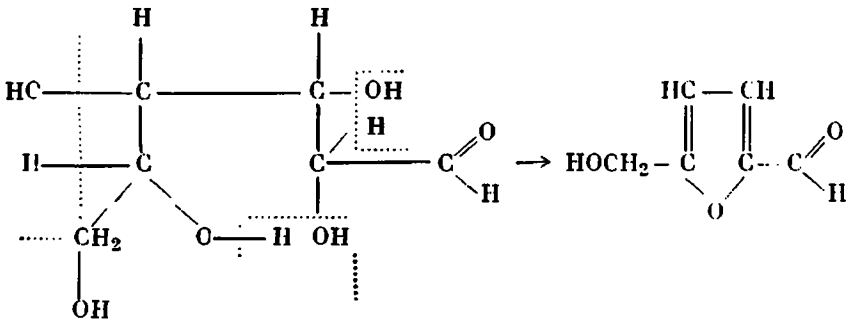
Glucose or *saccharose*, 5 per cent solution.

Place 1 ml of sugar solution into a test tube and add 2 ml of concentrated hydrochloric acid. Boil the mixture over a burner for 1-2 minutes: the liquid darkens and brown flakes precipitate. Cool the mixture, transfer 0.5 ml into another test tube and dilute with 10-12 volumes of water to prepare a pale brown cloudy solution. Pass it through a pleated filter, and add 0.5-1 ml of iodine solution to the clear, pale yellow filtrate. Finally add dilute alkali solution, drop by drop, until the colour vanishes.

Simultaneously carry out the test with a sample of the original sugar solution that was not boiled with hydrochloric acid. Add iodine and alkali to this solution and note in which of these two solutions iodoform is formed in the cold. The formation of iodoform manifests itself as a yellow turbidity, and a specific odour can be felt.

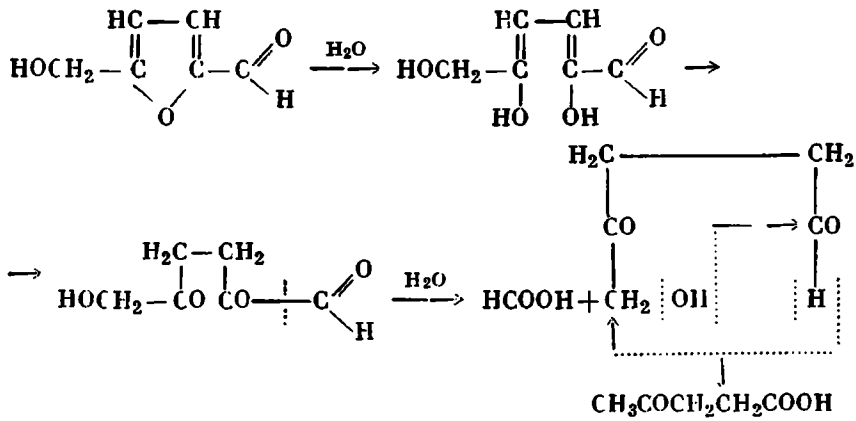
Strong mineral acids react with aldo- and ketohexoses to give, among other products (see Experiment 121), hydroxymethylfurfural.

For the case with aldohexoses, the reaction is as follows:



Ketoses in this reaction are first isomerized and the carbonyl group moves to the end of the chain. Hydroxymethylfurfural is then also produced.

As hydroxymethylfurfural reacts with the mineral acid (or strong organic acid, e.g. oxalic), it joins water with opening of the furane ring. The unsaturated aldehyde-alcohol, dienol, which is first produced, is then isomerized into diketone that decomposes with joining water and new re-grouping, in which the hydrogen atom and the hydroxyl group change places. The end products in this chain of complicate conversions are formic and levulinic acids:



Levulinic acid (m.p. 37 °C) derives its name from 'levulose' from which it was obtained by a similar way. Levulose (fructose) forms levulinic acid by heating with dilute hydrochloric acid. In the reaction with concentrated hydrochloric acid, fructose undergoes deeper decomposition to give dark coloured products (see Experiment 121). Glucose is stabler in these conditions; it almost does not react with dilute hydrochloric acid and only gives levulinic acid with concentrated HCl.

The formation of iodoform proves the presence of a compound having the atom grouping CH_3CO-. In our case this is levulinic acid (cf. Experiment 73).

The starting solution of sugar gives iodoform reaction neither at room temperature nor on heating.

129
Oxidation of Monosaccharides with Bromine Water

REAGENTS

Glucose and *fructose*, 2 per cent solutions.

Bromine water, saturated solution prepared immediately before the test.

Ferric chloride, solution coloured violet with phenol (see Experiment 79).

Carry out simultaneously the tests with glucose and fructose.

Place 1 ml of each sugar solution into two separate test tubes and add 6 ml of bromine water into both. Heat the mixtures on a boiling water bath for 15 minutes. If the colour of the solutions persists, boil the solutions over a burner for 30-60 seconds, until they become clear.

Cool both solutions in water to room temperature, add a few drops of ferric chloride solution and compare the colour of liquids.

Sugars are rather slowly oxidized with bromine in an acid medium. Aldohexoses turn into polyoxyacids, first monobasic and then dibasic.

In the conditions of the experiment, glucose gives monobasic gluconic acid:

$$Br_2 + H_2O \rightleftharpoons HBr + HOBr$$

$$CH_2OH(CHOH)_4C\begin{matrix}\diagup\!\!\!\diagup O \\ \diagdown H\end{matrix} + HOBr \rightarrow CH_2OH(CHOH)_4COOH + HBr$$

Gluconic acid has five hydroxyl groups. One of them is in the α-position to the carboxylic group. The acid gives the colour reaction with ferric chloride, characteristic of α-oxyacids (see Experiment 79).

Ketohexoses are more stable to oxidants. Fructose is almost not oxidized in the conditions of the experiment. When oxidized more energetically, ketohexoses decompose to give oxyacids having smaller number of carbon atoms.

130
Oxidation of Aldose and Ketose with Iodine

REAGENTS

Glucose and *fructose*, 2 per cent solutions.

Carry out simultaneously the tests with glucose and fructose. Place 3 ml of each sugar solution into two separate test tubes and add 0.5 ml of iodine solution into both. To measure out iodine, use a pipette or a burette. Add equal number of drops of dilute alkali solution to both test tubes, trying to do it simultaneously, until the colour vanishes. Note the time when the alkali is added, and place the test tubes in the stand. In 7-8 minutes, add 0.5 ml of dilute sulphuric acid to both solutions and compare the colours that develop.

In the presence of excess alkali, the equilibrium of the reversible reaction

$$I_2 + 2NaOH \rightleftharpoons NaI + NaOI + H_2O$$

strongly shifts to the right, and the iodine-coloured solution is decolourized. A strong oxidant, hypoiodite, appears in the system. Aldehydes are oxidized easier than ketones. The difference in the oxidation rates of aldo- and ketohexoses is less marked, especially in an alkaline medium, but in the conditions of the experiment it is quite distinct.

Adding acid, which binds alkali, shifts the equilibrium to the left. But in the course of the experiment, the greater part of hypoiodite in the solution of aldose, glucose, is spent for oxidation of glucose to gluconic acid (cf. Experiment 129), and as the mixture is acidified, free iodine is almost not formed. Ketose, fructose, is oxidized slower. In the same period of time, the hypoiodite does not disappear from the solution, and as acid is added, free iodine precipitates.

Oxidation with iodine in an alkaline solution is used for quantitative determination of aldoses in a mixture of sugars.

On longer standing, hypoiodite is gradually spent for oxidation of fructose as well.

131
Oxidation of Sugars by Dehydrogenation

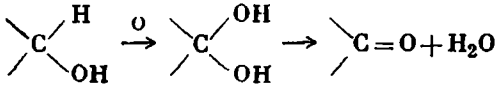
REAGENTS

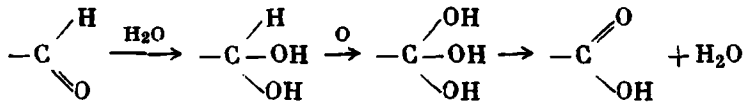
Glucose, or other *reducing sugar*, and *saccharose*, 1-2 per cent solutions.

Methylene blue, very dilute, bright blue solution (see Experiment 249)

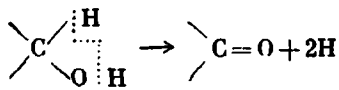
Place 3-4 ml of each sugar solution into separate test tubes and add 1 ml of methylene blue and 0.5 ml of dilute alkali into each solution. Place the test tubes on a hot water bath for a few minutes. Note, in which test tube the bright blue colour of the solution turns pale yellow.

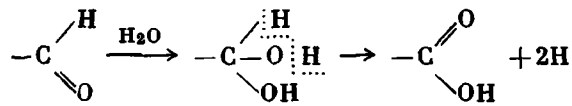
Oxidation of organic compounds, e.g. alcohols or aldehydes, is often regarded as their reaction with oxygen, either free or taken from oxidants:





But in many cases, alcohols are oxidized to aldehydes (or aldehydes are oxidized to acids, etc.) in the absence of oxygen, by eliminating hydrogen atoms from the molecule of the original substance





Oxidation by dehydrogenation is sometimes accompanied by liberation of free hydrogen (see Experiment 57), but Wieland showed that such oxidation usually requires the presence of substances binding the eliminated hydrogen, the hydrogen acceptors, e.g. palladium metal.

Methylene blue (see Experiment 249) easily joins the eliminated hydrogen to turn into a colourless leuco compound. Methylene blue is therefore often used as indicator of the dehydration reaction (decolouration of the blue solution).

In accordance with its structure, saccharose is stabler to oxidants (see Experiment 125) and is dehydrogenated with greater difficulty than reducing sugars, e.g. glucose. The yellow colour of glucose solution (after decolouration of the methylene blue dye) is due to the reaction of sugar with alkali on heating (see Experiment 124). Sugar is not dehydrogenated in the absence of alkali.

132
Oxidation of Glucose with Atmospheric Oxygen in the Presence of Hydrogen Acceptors

REAGENTS

Glucose, 1-2 per cent solution.
Indigo carmine, 0.1 per cent solution.
Methylene blue, 0.1 per cent solution.

A. Place 5-6 ml of glucose solution into a test tube, add 0.5-1 ml of soda solution and a few drops of indigo carmine. Heat the bright blue solution to boiling; the solution turns yellow. Shake the hot liquid: it turns blue but then soon becomes yellow again. Cool the yellow solution without jolting in cold water: the yellow colour of the solution persists, but when the test tube is shaken, the liquid quickly turns green and then blue. When the solution is heated again, the yellow colour is restored.

B. Place 2 g of glucose into a 100-200 ml flask and dissolve them in 50 ml of water. Add 3 ml of concentrated alkali and then, with shaking, a small quantity of methylene blue, until the solution becomes bright blue. The solution decolourizes on standing for 2-3 minutes. Shake the flask energetically until it begins foaming: the liquid again turns blue. It is decolourized again on standing.

The colour change in tests A and B can be observed many times at a run.

Glucose can be dehydrogenated in an alkaline medium to convert into gluconic acid (see Experiment 131):

$$CH_2OH(CHOH)_4CHO + H_2O \longrightarrow CH_2OH(CHOH)_4COOH + 2H$$

In test A, the acceptor of hydrogen (i.e. the substance that binds hydrogen) is indigo carmine, which is a sulpho derivative of the heterocyclic compound, indigo (see Experiment 244). Blue indigo carmine combines with hydrogen to give a yellow leuco compound (see Experiment 246) that is easily oxidized by air to form the starting indigo carmine and water. If the hot alkaline solution still contains glucose, the process is repeated. Thus, glucose is finally oxidized to gluconic acid by atmospheric oxygen, indigo carmine

(promoting the reaction) being a sort of transmitter of hydrogen to oxygen. In the absence of indigo carmine, hydrogen that is eliminated during dehydrogenation of glucose is oxidized by atmospheric oxygen very slowly, and the reaction is practically absent.

Since indigo carmine is recovered in the course of the reaction, i.e. not spent in the reaction, it is a typical catalyst in the given conditions, and the entire system is a model of oxidative enzymatic process.

In test B, the role of the catalyst, trasmitter of hydrogen, is performed by another dye, methylene blue (see Experiments 131 and 249, and explanations to them). The process occurs in a stronger alkaline medium, at room temperature. The colour change is even more distinct.

133
Selivanov's Test for Ketoses

REAGENTS

Glucose, *fructose*, *maltose* (*lactose*), and *saccharose*, 2 per cent solutions.

Selivanov's solution (solution of 0.01 g of resorcinol in a mixture of 10 ml of water and 10 ml of concentrated hydrochloric acid). Prepare the solution immediately before the test.

Carry out simultaneously several tests with various sugars.

Place 0.5-1 ml of each sugar solution in separate test tubes and add 2 ml of Selivanov's reagent into each test tube. Immerse them in boiling water for 2 minutes.

Solutions of some sugars are soon coloured bright red. If red solutions are then heated over a burner to boiling, they become cloudy and a coloured substance precipitates. Solutions of other sugars become only slightly yellow or pink.

When heated with hydrochloric or sulphuric acid, hexoses form, among other products (see Experiments 120 and 121), hydroxymethylfurfural, which reacts with resorcinol to give a brightly coloured condensation product, $C_{12}H_{10}O_4$. In conditions of the experiment, ketoses convert into hydroxymethylfurfural 15-20 times faster than aldoses, and this accounts for the rapid development of the colour and its intensity in solutions of fructose and saccharose.

The reaction was discovered by F. F. Selivanov in 1887. It can be used for rapid detection of ketohexoses (either free or bound in disaccharide molecules) in a mixture of sugars. Disaccharides are partly hydrolysed in this reaction to give free monosaccharides.

The Selivanov reaction can also be carried out in alcohol solutions. It is a modification of the Molisch general test for carbohydrates

(cf. Experiment 120), in which diphenylamine is often used instead of resorcinol. In this case the blue colour is more intense, which is more convenient for quantitative colorimetric determinations of fructose.

134
Formation and Properties of Calcium Saccharates

REAGENTS

Glucose.

Saccharose.

Lime milk (10-15 per cent aqueous suspension of $Ca(OH)_2$; prepare the reagent immediately before the experiment). The reagent should not contain much calcium carbonate.

Carbon dioxide (from a gas cylinder or a Kipp generator).

Hydrochloric acid, standard 0.1-0.2 *N* solution.

Carry out simultaneously the tests with glucose and saccharose. Dissolve 1 g of sugar in 5-6 ml of water. Shake the lime milk and add it to the sugar solution, drop by drop, at room temperature, with shaking. The first drops of lime milk are dissolved completely and the solution remains clear. Add lime milk until a considerable amount of precipitate appears on standing. The precipitate should not disappear on shaking.

In 3-5 minutes, pass the mixture through a small pleated filter and divide the clear filtrate into three parts.

A. Pass a slow current of carbon dioxide into one sample of the filtrate, using a thin glass tube with a drawn end. Calcium carbonate precipitates. If carbon dioxide is passed for a long time, the precipitate can dissolve, calcium bicarbonate is formed.

B. Add a drop of phenolphthalein to another portion of the filtrate, and titrate the mixture with standard hydrochloric acid from a burette. Add the acid drop by drop until the crimson colour vanishes. One millilitre of 0.1 *N* HCl is equivalent to 2.8 mg of calcium oxide.

C. Heat the third portion of the filtrate in a test tube over a burner until it starts boiling: one of the two solutions first becomes yellow, then brown. A dark coloured precipitate falls out on standing.

The other solution remains colourless on boiling. Only a small white precipitate of crystalline tricalcium saccharate falls out. Cool the test tube in a beaker with water and shake: the precipitate disappears. If the solution is heated again, the precipitate re-appears.

Like other compounds containing several hydroxyl groups in a molecule, sugars react with hydroxides of many metals to give stable alcoholates, usually soluble in water. Calcium hydroxide therefore dissolves in aqueous solutions of sugars much better than in pure water. (A saturated solution of calcium hydroxide in water contains only 1.26 mg of CaO in 1 ml at 20 °C; the solubility rapidly decreases with growing temperature.)

The composition of the formed alcoholates (calcium saccharates) is different. Sugars are very weak acids (e.g. the ionization constant of glucose is only 6×10^{-13}) and are therefore displaced from calcium saccharates even by carbonic acid. This is used in industry for purification of beet sugar. For the same reason calcium saccharate solutions react strongly alkaline. In the presence of an indicator, the entire calcium bound in a saccharate can be titrated with acid. Titration of saccharate solutions is used in some titrimetric methods of analysis.

The strong alkaline reaction of the solution is responsible for instability of calcium alcoholates of those sugars that have free glucoside hydroxyl groups in their molecule (reducing sugars, see Experiment 125). When heated, their solutions turn brown and give a complicate mixture of products. On the contrary, saccharose forms more stable calcium saccharates. Tricalcium saccharate is especially interesting. Its solubility in water sharply decreases with rising temperature. Heating precipitates crystals of $C_{12}H_{22}O_{11} \cdot 3CaO \cdot 3H_2O$ from solution, but as the mixture is cooled, the crystals dissolve again.

135
Hydrolysis (Inversion) of Sucrose

REAGENTS

Sucrose, 2 per cent solution.

Place 8-10 ml portions of sucrose solution into two separate test tubes and add 3-4 drops of dilute sulphuric acid or hydrochloric acid into one of them. Heat both on a water bath for 10-15 minutes, then cool, and pass each solution through reactions with alkali (see Experiment 124), methylene blue (Experiment 131), a cupric salt (Experiments 125 and 126), ammoniacal silver oxide solution (Experiment 127), and α-naphthol (Experiment 120).

Note the different results of the tests with sucrose solutions with and without acid. There should be no difference in the reaction of both solutions with α-naphthol.

Sucrose molecule contains neither free glucoside hydroxyls nor carbonyl groups, and thus it differs from monosaccharides and most disaccharides with respect to its reaction to many reagents.

Sucrose undergoes hydrolysis to give glucose and fructose:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Like in many other cases (see Experiment 93), hydrolysis of sucrose is significantly accelerated by the catalytic action of hydrogen ion, i.e. strong acids. Hydrolysis of sucrose changes the direction of rotation of the polarization plane of light, i.e. inverts the rotary power, and the reaction is therefore named 'inversion'.

The reactions mentioned in the experiment reveal the appearance, in sucrose solution, of strongly reducing products of its hydrolysis, viz., glucose and fructose. The course of the reaction with α-naphthol, which is the general reagent for hydrocarbons, does not change after hydrolysis.

136
Preparing Mucic Acid

REAGENTS

Milk, fresh.
Lactose or *galactose*.

A. Mix, in a beaker or a dish, 100 ml of cow milk with 100 ml of water and add, with stirring, concentrated acetic acid (about 0.5 ml) to coagulate proteins (see Chapter 21). In 10-15 minutes, pass the liquid through a cloth freely folded in a funnel.

Add 1-2 ml of dilute alkali solution and 2-3 drops of copper sulphate to a few millilitres of the slightly cloudy filtrate. Heat the mixture first to boiling: the blue colouration disappears, and a yellow or red substance precipitates (see Experiment 125). This indicates the presence of reducing sugar in solution; in our case this is lactose.

Place the remaining filtrate (100-150 ml) into a beaker or a flask, add 20 ml of concentrated nitric acid, and heat the mixture on a wire gauze over a burner until it starts boiling. Protein flakes precipitate again, and the mixture turns yellow (see Experiment 284). Pass the hot liquid through a pleated paper filter into a porcelain dish. Evaporate the clear filtrate in the HOOD, heat first over a burner, on a hotplate, or a sand bath to evaporate half liquid volume, and then on a boiling water bath, with stirring, to 15-20 ml. Cool the obtained liquid and allow to stand for 15-20 minutes.

Mucic acid precipitates as white fine crystals. Filter the precipitate with suction, wash with cold water, and dry.

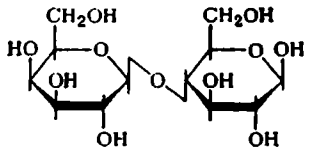
B. Use crystalline lactose for the test. Dissolve 1 g in 7-8 ml of water. Use a small portion of the obtained solution in the test for reducing sugars (see above). Add 3 ml of concentrated nitric acid to the remainder and evaporate the mixture in a dish in the HOOD. Heat first over a burner to reduce to a small volume, and then on a water bath, almost to dryness. Cool the dish and separate the precipitated mucic acid (see above).

Galactose can be used instead of lactose. The yield of mucic acid is doubled.

The product can be used in Experiment 240.

To purify mucic acid, dissolve it in a small volume of dilute alkali and precipitate again by acidifying the solution with dilute sulphuric acid.

Milk contains about 4-5 per cent of milk sugar, lactose ($C_{12}H_{22}O_{11}$), which is biose consisting of galactose and glucose residues



Lactose has a free glucoside hydroxyl and therefore reduces cupric salts in an alkaline solution.

Acidifying with acetic acid precipitates the greater part of proteins from milk. Further addition of nitric acid with heating completes the precipitation of proteins. As the strongly acid liquid is further heated lactose is hydrolysed to give two monosaccharides, glucose and galactose. With evaporation of water, concentration of nitric acid increases and monosaccharides are oxidized first to monobasic acids, $CH_2OH(CHOH)_4COOH$, gluconic and galactonic, and then to dibasic acids, $HOOC(CHOH)_4COOH$, saccharic and mucic.

Unlike other products of sugar oxidation, mucic acid is sparingly soluble in water (0.3 parts by weight in 100 volumes of cold water and 1.7 parts in 100 volumes of hot water). Therefore, precipitation of mucic acid positively indicates the presence of galactose, and hence lactose, in the oxidized mixture. This method can be used to detect galactose, contained in water in as small concentration as 1 : 1000.

As dilute solutions of mucic acid are slowly cooled, the acid precipitates in the form of beautiful needles.

The symmetry of steric structure of mucic acid accounts for the absence of optical activity through inner compensation.

137
Reactions of Starch

REAGENTS

Starch.
Ethyl alcohol, crude or rectified.

Place 1 g of dry starch in a test tube, add 5-6 ml of water, shake, and allow to settle for 1-2 minutes. Decant the water, and wash the starch with new portions of water two or three times. Add the last portion of water and shake well. Pour the starch suspension into 50 ml of water heated to boiling in a beaker or a flask. Almost clear, slightly opalescing starch solution is formed.

Cool the solution and carry out the following tests.

A. Place 1-2 ml of starch solution into a test tube and add a drop of iodine. Heat the intensely blue liquid: the colour vanishes, but re-appears on cooling.

B. Mix another sample of starch solution (1-2 ml) with 1 ml of alcohol and add iodine: the mixture becomes only slightly brown.

C. Add a few drops of dilute alkali to 1-2 ml of starch solution and heat the mixture to boiling: no changes, except slightly yellowing, can be noticed.

D. Add a few drops of alkali and 1-2 drops of copper sulphate to 1-2 ml of starch solution and heat on a boiling water bath for 2-3 minutes: the solution remains almost colourless. Blue particles of non-dissolved copper hydroxide turn black on heating. Neither red nor yellow precipitate is formed.

Natural starch contains two polysaccharides, amylose and amylopectin, the molecules of which are constructed out of residues of disaccharide, maltose. Maltose remainders are arranged in amylose in the form of a chain, while in amylopectin they form a more intricate structure. Part of hydroxyl groups in the amylopectin molecule is esterified by phosphoric acid.

The proportion of amylopectin in natural starches is much greater than of amylose. The molecular mass of amylopectin is over 1,000,000, while that of amylose does not exceed 200,000. Starch is practically insoluble in cold water, and it forms a colloidal jelly in hot water. When stored for a long time, starch solution quality is much deteriorated by the propagating microorganisms. This can easily be prevented by adding traces of mercury or silver salts.

Amylose reacts with iodine to give a clear blue colour; amylopectin produces blue-violet colouration. The development of colour is accounted for, according to the modern views, by the formation of molecular compounds of iodine with amylose and amylopectin. In amylose, unbranched chains of glucose residues take the confi-

guration of a helix with an open core, the hollow of which is filled with iodine molecules (one iodine molecule per one glucose residue). The formed inclusion compound (clathrate) has the general composition $C_6H_{10}O_5 \cdot I_2$. Amylopectin also adsorbs iodine. Decolourizing of the complex with heating, and in the presence of alcohol, makes it difficult to use starch as indicator in iodometric titration. The reaction with iodine (Gautier, 1814) can detect even 0.01-0.05 mg of starch in 1 ml of solution. Bromine gives only slight yellow colour with starch.

The long chain-like molecules of amylose and amylopectin contain free glucoside hydroxyl groups only at the ends of the chain, i.e. their number in the molecule is very small, and starch does not therefore give sufficiently distinct reactions with alkali (see Experiment 124) or copper salts (Experiment 125).

Commercial starch often contains soluble impurities that can be resinified by alkalis and reduce divalent copper. To ensure more distinct results in tests C and D, wash starch to remove soluble impurities before preparing the starch solution.

138
Formation of Dextrin and Its Reactions

REAGENTS

See the previous experiment.

Place about 0.5 g of dry starch into a dry test tube, and heat very carefully, with constantly shaking the test tube, over a burner until the powder begins to turn yellow. Allow the test tube to cool and add 5-6 ml of cold water to the formed dextrin. Shake the mixture energetically for 1-2 minutes and pass through a paper filter. Divide the clear filtrate into four portions and carry out the tests described in the previous experiment: with iodine, alcohol, alkali with heating, and with a cupric salt in an alkaline solution with heating. The difference between starch and dextrin in their attitude to these reagents is quite apparent.

A. Iodine colours dextrin solution brown or reddish.

B. Alcohol precipitates dextrin flakes from its aqueous solution.

C. When boiled with alkali, dextrin solution turns bright yellow or brown.

D. Divalent copper is reduced by dextrin to monovalent copper, and the reaction mixture reddens on heating.

When heated to 200-250 °C, large molecules of starch (amylose and amylopectin) fall into smaller molecules to form a mixture of dextrins. In contrast to starch, the products of its decomposition

are quite readily soluble in water, they contain a greater number of free glucosidic hydroxyls and, in Experiments 138, C and D, show clearly reducing properties. Experiment 138, A (iodine test) allows one to judge on the relative size of dextrin particles. As they diminish (in other words, as starch undergoes deeper decomposition), the colour changes from blue, through violet and reddish brown, to pale yellow, and finally vanishes completely.

139
Hydrolysis of Starch by Acids

REAGENTS

Starch.
Calcium carbonate, powder.

Prepare starch solution from 1 g of starch (see Experiment 137). Place 15-20 ml of starch solution into a beaker or a flask, add 1 ml of dilute sulphuric acid, and boil the mixture for 5-10 minutes. At 1-2 minute intervals, take small samples (1-2 ml) of the hot liquid into separate test tubes, cool in water, add a drop of iodine solution, and place the test tube in the stand. The colour of solution gradually changes in the series.

When iodine fails to develop the colour in a new sample, boil the solution for another 5-6 minutes, then cool, and add (gradually and with shaking) 2 g of calcium carbonate. When foaming stops, pass the hot mixture through a pleated filter to collect 10-20 ml of clear filtrate. Test the contained solution for monosaccharides and compare the changes with the results of Experiment 137 (with the original starch).

Evaporate 10-15 ml of the filtrate in a porcelain dish, and finally on a boiling water bath to prevent burning, to obtain a few drops of a thick, yellow, sweet syrup.

Hydrolysis of starch, like of other compounds (see Experiments 93 and 135) is much accelerated in the presence of acids. The subsequent deep hydrolysis of starch gives a series of products. The first are dextrins (Experiment 138), then follows disaccharide maltose, $C_{12}H_{22}O_{11}$, and finally monosaccharide D-glucose.

The general equation of hydrolysis of starch is as follows:

$$(C_6H_{10}O_5)_n + nH_2O \longrightarrow nC_6H_{12}O_6$$

Calcium carbonate is added to remove sulphuric acid from the solution

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

The sparingly soluble calcium sulphate (about 2 g per litre) and excess calcium carbonate are separated by filtration. Any strong acid, e.g. hydrochloric acid, can be used to accelerate hydrolysis of starch, but it is easier to separate the hydrolysate from sulphuric than from hydrochloric acid.

Hydrolysis of starch with acids is used in industry to obtain syrup. The syrup contains not only glucose, but also varying quantities of maltose and dextrins.

Starch was first hydrolysed in the presence of acid by the Russian academician K. S. Kirchhoff in 1811.

140
Hydrolysis of Starch by Saliva

REAGENTS

Starch.

Saliva, fresh solution.

To prepare the saliva solution, rinse the mouth for about a minute with 20-30 ml of distilled water and pass the liquid through a pleated filter. The salivation can be stimulated by chewing a piece of paraffin wax.

Carry out the test simultaneously in three test tubes. Place 5-ml saliva solution portions into two test tubes and 5 ml of distilled water into the third test tube (control). Heat the saliva solution in the second test tube to boiling. Boil for 1-2 minutes holding the test tube so that not only the liquid but also the foam is heated by the flame of the burner. Cool the test tube.

Prepare 20-25 ml of starch solution (Experiment 137) from 0.5 g of starch. Add 5 ml of the cooled starch solution into each test tube, shake all of them, and place simultaneously into a beaker containing water heated to 40 °C. Note the time. Take 0.5-1 ml samples out of each of the three test tubes at 1-2 minute intervals and add a drop of iodine into each sample.

Continue the hydrolysis for 10-12 minutes until iodine produces no colour reaction in one of the tubes. Test the solution in each test tube for the presence of reducing sugars (reaction with a copper salt in an alkaline solution with heating, see Experiment 125). Note the difference in the results.

Saliva contains the enzyme ptyalin (amylase), which quite energetically catalyses hydrolysis of starch. Unlike acid hydrolysis (cf. Experiment 139), the hydrolysis of starch by ptyalin proceeds only to disaccharide maltose.

The reaction with iodine in the first test tube (with non-heated saliva) very soon shows conversion of starch into dextrins (see Experiment 138). In 5-6 minutes the solution is no longer coloured by iodine, and the reaction with copper salts (Experiment 125) detects reducing sugars in the solution.

All enzymatic processes are characterized by a certain optimum of temperature, which in our case is close to 40 °C. Heating to 100 °C decomposes (denaturates) the enzyme, which is a protein, and saliva no longer hydrolyses starch. Therefore, no hydrolysis is detected in the second (boiled saliva) or the third (control) test tube.

Enzymatic hydrolysis of starch to maltose by the action of amylase (out of malt) was discovered by K.S. Kirchhoff (1814).

141
Reaction of Cellulose with Alkali

REAGENTS

Filter paper.

Fix two test tubes in the stand and fill one of them, almost to the full capacity, with water and the other with concentrated alkali. Cut out two strips of filter paper of equal size. The length of the strips should exceed the height of the test tubes by 2-3 cm and the width should be 1.5-2 cm. Fold the strips in two along the longitudinal axis so that they can enter the test tube. Immerse one strip into water to reach the bottom of the test tube, and the other into alkali and keep for 5-7 minutes. Meanwhile prepare a third test tube containing dilute hydrochloric acid.

Remove the paper strip from water, press out excess liquid on a sheet of filter paper, and allow to dry in the air. Remove the other strip from the alkali, shake off alkali drops, dip into water, then into hydrochloric acid, again into water, and press out excess liquid. Allow both strips to dry and compare their lengths, densities, and the character of the surfaces.

Caustic alkali is absorbed by cellulose from concentrated solution and is partly bound with it. Cellulose strongly swells, its fibres thicken, and shorten. Subsequent washing removes alkali. This treatment, known as mercerization (J. Mercer, 1848), improves cotton lustre and increases attraction for colouring dyes.

142
Dissolution of Cellulose in Schweitzer's Reagent

REAGENTS

Cotton wool, or *filter paper.*
Schweitzer's reagent.

To prepare the reagent, first obtain copper hydroxide by precipitating it from a 5 per cent solution of copper sulphate with alkali taken in excess. Filter out the precipitate, wash it several times with water, press out excess liquid on a sheet of filter paper, and dissolve immediately in the least possible quantity of concentrated aqueous ammonia. Another method consists in dissolving dry copper carbonate in concentrated aqueous ammonia solution. Pass the dark blue solution thus obtained through a glass wool filter.

Place 3-4 ml of clear Schweitzer's reagent in a test tube and add pieces of filter paper or cotton wool. Shake the contents: cellulose fibres are rapidly disjoined and almost completely dissolved to form a viscous liquid. Transfer about 1 ml of the clear thick solution into another test tube, add 4-5 ml of water, and transfer the obtained solution into a beaker or a wide test tube containing 10-12 ml of dilute hydrochloric acid. The mixture is almost immediately decolourized and white jelly-like free cellulose precipitates.

Carry out the sample of the acid solution through the test for reducing sugars (Experiment 125).

An ammoniacal copper solution was proposed by Schweitzer. It contains the complex base $[Cu(NH_3)_4]^{2+}(OH^-)_2$ in solution form. The molecule of cellulose, $(C_6H_{10}O_5)_m$, consists of a great number of glucose residues, each having three free hydroxyls. When cellulose is dissolved, hydrogen atoms in two hydroxyls are replaced by a copper atom, while the hydrogen atom of the third hydroxyl group is ionized. For this reason, although the glucose residues are still joined between themselves, they form anions $(C_6H_7O_6Cu)^-$ and hydrogen cations that are bound by ammonia. Cellulose solution in Schweitzer's reagent therefore contains copper in both anions and cations.

Acids decompose copper complexes to bind copper and ammonia. The regenerated cellulose is quite similar to the original with respect to its composition, but its fibrous structure, which is characteristic of natural cellulose, is lost. Fibres of the required thickness can, however, be produced out of such regenerated cellulose. Cellulose can be isolated from Schweitzer's solution not only by acids but

by concentrated alkali and salt solutions as well. This method was first used to manufacture cuprammonium silk.

The sample of acid solution does not give the reaction for reducing sugars (see Experiment 125) hence cellulose is not hydrolysed in these conditions.

143
Conversion of Cellulose into Amyloid

REAGENTS

Filter paper.

Place 3 ml of water into a test tube, and carefully add with shaking 5 ml of concentrated sulphuric acid. Cool the hot liquid to room temperature in a beaker with water. Dip a strip of filter paper into about 70 per cent sulphuric acid thus obtained and keep for 10-15 seconds. Remove the strip and thoroughly wash in several portions of water (or in running water) to remove the acid. Finally rinse the strip in water containing small amounts of ammonia. Observe the differences in density and strength of wet paper in its acid-treated and untreated parts. Dry the paper: the differences become more distinct.

Place a drop of iodine solution at the point where the acid-treated and untreated parts of the paper border: observe the different colouration of the paper.

144
Dissolution and Hydrolysis of Cellulose by Acids

REAGENTS

Cotton wool, or *filter paper.*

Sulphuric acid, about 70 per cent solution (see the previous experiment).

Place 7-8 ml of cold 70 per cent solution of sulphuric acid into a test tube and add a piece of cotton wool or twisted filter paper. Shake for 1-2 minutes: cellulose fibres are first disjoined, and then almost completely dissolved to form a thick colourless solution.

Transfer half of the obtained solution into another test tube to mix it with five volumes of water: flakes of water-insoluble products of cellulose partial hydrolysis precipitate.

Heat the remainder of the solution for a few minutes on a hot water bath until it turns pale brown. Cool the solution and also mix with five volumes of water: flakes do not precipitate.

Place 1-2 ml of the obtained solutions into two separate test tubes, neutralize them with alkali, and test for the presence of reducing sugars (see Experiment 125). The solution obtained by hydrolysis of cellulose on heating reduces divalent copper much faster and more energetically.

Cellulose reacts with a sufficiently concentrated sulphuric acid first to esterify free hydroxyl groups of cellulose with formation of acid esters according to the general equation common for alcohols (see Experiment 41):

$$ROH + H_2SO_4 \longrightarrow ROSO_2OH + H_2O$$

The oxygen bonds between glucose residues in cellulose are simultaneously hydrolysed to form smaller particles; hence the dissolution of cellulose.

Concentrated sulphuric acid acts on cellulose too energetically. The 70 per cent acid can act for a short period of time in the cold to dissolve only the superficial structures of cellulose (Experiment 143), and to cement the fibres of cellulose by the product of its partial hydrolysis, amyloid, into a dense mass. Paper thus treated is known as vegetable parchment.

Amyloid is insoluble in water and, unlike cellulose, is coloured blue by iodine. Here it behaves like starch, hence the name amyloid (Latin *amylum*, starch).

Longer action of the acid causes complete dissolution and a deeper hydrolysis of cellulose (Experiment 144).

High-molecular products of cellulose hydrolysis that are formed in the beginning of the process (amyloid, hydrocellulose, etc.) can be precipitated if the solution is diluted with water. Heating the acid solution promotes further hydrolysis and formation of simpler substances, hexa-, tetra- and trisaccharides. Finally, cellulose is hydrolysed into cellobiose and glucose. These compounds are soluble in water and contain free glucoside hydroxyls. This accounts for energetic reduction of divalent copper in an alkaline medium.

145
Preparing Cellulose Nitrates

REAGENTS

Cotton wool, better hygroscopic.
Ethyl ether and *ethyl alcohol* (rectified), 3 : 1 mixture.

Place 4 ml of concentrated nitric acid into a wide test tube and carefully add, with shaking, 8 ml of concentrated sulphuric acid.

The mixture becomes hot. Cool it, and add a small clot of cotton wool with a glass rod provided with a hook. Carefully stir the test tube contents and heat on a water bath at a temperature of 60-70 °C.

In five minutes, remove the cotton and wash in water, changing it several times (better under a tap). Press out excess water first by hand, then on a filter paper, and dry in a porcelain dish on a boiling water bath.

The resultant pale yellow fibrous product is *colloxylin* or guncotton.

Divide the product into two parts.

A. Using crucible tongs put a piece of the obtained colloxylin into the flame of a burner: it flashes.

B. Place the remainder into a test tube and add 1-2 ml of an ether-alcohol mixture: colloxylin gradually swells to form a colloidal solution, *collodion*. Pour the collodion on a glass plate: when the solvent is all evaporated, a film remains on the glass. Take it by forceps and put into the flame of a burner: the film burns slower than colloxylin in test A.

For the purpose of comparison, carry out tests A and B using clots of cotton wool of the same size but untreated with the acid mixture.

At the end of the experiment, make sure that the entire manufactured colloxylin is destroyed (burnt or dissolved). Do not keep it in the laboratory.

Cellulose reacts with a mixture of nitric and sulphuric acids to the effect of esterification of free hydroxyl groups of cellulose with nitric acid. Each glucose residue ($C_6H_{10}O_5$) in the complicate molecule of cellulose contains three hydroxyl groups, and full esterification of cellulose (with respect to one glucose residue) occurs according to the equation:

$$C_6H_{10}O_5 + 3HNO_3 \longrightarrow C_6H_7O_2(ONO_2)_3 + 3H_2O$$

The obtained trinitrocellulose, *pyroxylin*, is an important explosive. In conditions of the experiment described above, the reaction does not proceed to the end and the product obtained is *colloxylin*. It contains mainly cellulose dinitrate, $C_6H_8O_3(ONO_2)_2$. Colloxylin is not explosive.

The process of formation of cellulose nitrates was studied in detail and methods of their industrial utilization were developed by D. I. Mendeleev.

Cellulose nitrates decompose thermally with liberation of much heat without access of atmospheric oxygen. The decomposition is accompanied by evolution of large volumes of gas. The decomposition of pyroxylin can be described by the following formula:

$$2C_6H_7O_2(ONO_2)_3 \longrightarrow 6CO_2 + 6CO + 4H_2O + 3N_2 + 3H_2$$

When heated in a closed space, or under the effect of detonation, pyroxylin explodes to form the same gaseous products.

Organic solvents, such as acetone, chloroform, ethyl acetate, ether-alcohol mixture, dissolve cellulose nitrates or they swell in them to form jelly-like substances that are easy to process and use.

146
Preparing Cellulose Triacetate and Its Properties

REAGENTS

Cotton wool, or *filter paper*
Acetic anhydride
Chloroform.
Acetone.

A. Mix 5 ml of acetic anhydride, 5 ml of glacial acetic acid, and 1-2 drops of concentrated sulphuric acid in a test tube. Soak 0.3-0.5 g of cellulose in water for 3-5 minutes, press out excess moisture, loosen by fingers, and add to the mixture. Using a glass rod push the cellulose clot to the test tube bottom, and leave the rod in the test tube. Place the test tube on a cold water bath. In 5-10 minutes, when liberation of heat stops, transfer the test tube onto a hot water bath, and stir its contents by the rod to complete dissolution of cellulose. As a rule, the dissolution completes very soon. Discharge the homogeneous liquid in a thin jet into a beaker, containing 250-300 ml of cold water, with stirring. Separate the precipitated flakes on a filter with suction (through filter paper or cloth). Press out liquid from the obtained mass, loosen it and dry in a dish on a boiling bath or in a drying cabinet. The yield is 100-120 per cent of the starting cellulose. The amorphous material can easily be ground into a powder.

B. Mix a small portion of dry cellulose acetate with 1-2 ml of acetone and heat the mixture for a few minutes until it gently boils. Decant the obtained solution onto a watch glass and allow acetone to evaporate. Note whether or not a film is formed.

C. Dissolve the remaining (greater) part of the cellulose acetate in 1-2 ml of chloroform with gently heating. Transfer the thick liquid onto a flat glass plate measuring minimum 10 × 10 cm, and allow to stand for a few minutes until the liquid is all dried. Now carefully wet the glass with water and remove the film. Dry the film in filter paper. Take part of the film and try it for combustibility in the flame of the burner. Test the starting cellulose for solubility in chloroform.

Cellulose reacts with acetic anhydride in the presence of a catalyst (concentrated sulphuric acid) to give the product of esterification (acetylation) of cellulose, which in our case is predominantly the triacetate:

$$C_6H_{10}O_5 + 3(CH_3CO)_2O \longrightarrow C_6H_7O_2(OCOCH_3)_3 + 3CH_3COOH$$

Cellulose triacetate is readily soluble in chloroform and tetrachloroethane, worse in acetone; it is insoluble in water. Cellulose diacetate well dissolves in acetone. Unlike cellulose nitrates, cellulose acetates burn with great difficulty, and hence are not explosive or inflammable. Cellulose acetate is therefore predominantly used in the manufacture of photographic films, rather than cellulose nitrate. Cellulose acetate is used as packing material for foods and other products, and also in the manufacture of acetate fibres.

CHAPTER TWELVE

AROMATIC HYDROCARBONS. THEIR HALOGEN-, SULPHO-, AND NITRO DERIVATIVES

Benzene, toluene, xylene (a mixture of the isomers where *m*-xylene usually predominates), styrene, and naphthalene can be used as representatives of aromatic hydrocarbons. Chlorobenzene and benzyl chloride can be used as their halogen-substituted compounds (for preparing styrene see Experiment 264).

Nitro compounds are prepared directly in the course of the experiment. Commercial nitrobenzene can be used for preparing dinitrobenzene in the laboratory.

The constants of some aromatic hydrocarbons and their derivatives are given in Table 10.

The benzene ring is designated by a hexagon with a circle inside (b), the symbol emphasizing the symmetry of the molecule and the evenly distributed, delocalized π-electrons. A carbon atom is understood at each point of the hexagon. In the absence of substitutes, a hydrogen atom is bonded to each carbon atom.

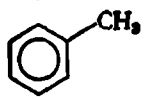
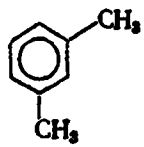
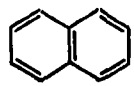
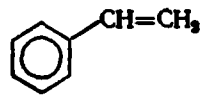
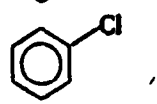
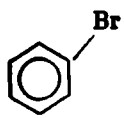
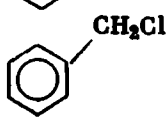
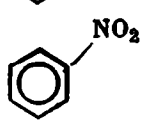
The designations of the benzene ring that were commonly used in the past, (a) and (c), are still in use in the modern literature.

a *b* *c*

Further in this book, the hydrocarbon residue (radical) R will be designated as Ar provided the character of the process is determined by the presence of an aromatic compound.

Table 10

Properties of Aromatic Hydrocarbons and Their Derivatives

Substance	Formula	M. p., °C	B. p., °C	Density, g/cc
Benzene		6	80	0.88
Toluene		—95	111	0.87
m-Xylene		—48	139	0.86
Naphthalene		80	218	1.15
Styrene		—31	145	0.91
Chlorobenzene		—45	132	1.11
Bromobenzene		—31	156	1.50
Benzyl chloride		—39	179	1.10
Nitrobenzene		6	211	1.20

147
Preparing Benzene from Benzoic Acid

REAGENTS

Benzoic acid.
Soda lime (if the reagent was long in storage, calcine it).

Thoroughly grind in a mortar 5 g of benzoic acid and 10 g of soda lime. Transfer the mixture into a test tube, close it with a plug through which a long tube is passed, and lower the tube outer end into a receptacle (test tube) cooled in a beaker with water and ice.

Heat the test tube over a burner, first gently, and then strongly: the mixture darkens and shrinks. Discontinue the heating when white spots on the surface of the mixture disappear.

The distillate in the receptacle segregates into two layers; the upper, benzene layer, is usually crystallized. See to it that the crystals do not clog the orifice of the outlet tube. Dry the upper layer of the distillate with a piece of calcium chloride and distil. Benzene distils completely at 79 to 80 °C. The yield is 2-2.5 g.

Decarboxylation of carboxylic acids, both fatty (see Experiment 23) and aromatic, i.e. elimination of carbon dioxide from carboxylic group by heating with alkali, is as a rule a smooth process. Non-substituted acids form mainly hydrocarbons:

$$C_6H_5COOH \xrightarrow[-CO_2]{} C_6H_6$$

Benzene thus prepared is quite pure. It does not contain thiophene, which is a common impurity in benzene recovered from coal-tar.

148
Bromination of Aromatic Hydrocarbons

REAGENTS

Benzene.
Toluene.
Naphthalene.

Use the HOOD.

Place 1 ml of benzene, 1 ml of toluene, and 0.5-1 g of naphthalene into three dry test tubes. Add 1 ml of bromine solution into each test tube and shake. Divide each mixture into two parts, by transferring part of solutions into dry clean test tubes. Place the former three test tubes into the stand, and heat the remaining test tubes to boiling. Place these test tubes in the stand as well.

The evidence of the bromination reaction is vanishing of the bromine colour and evolution of the fuming hydrogen bromide (Experiment 18).

Toluene is brominated in the cold slowly but quite distinctly. The reaction is fast with heating. Naphthalene is gradually dissolved and also brominated, slowly in the cold and faster with heating. Benzene is not brominated even with boiling (see explanations to Experiment 151).

149
Effect of Catalysts on Bromination of Aromatic Hydrocarbons

REAGENTS

Benzene.
Toluene.
Aluminium, amalgamated strip or wire.
Iron, filings.
Iodine, crystals.

To prepare amalgamated aluminium wire, or strip, clean the metal with abrasive paper, dip for a minute into a saturated solution of mercuric chloride (POISON!), rinse in water, then in alcohol and benzene, and use immediately. Use the HOOD.

A. Carry out simultaneously the experiment with benzene and toluene. Mix 2-3 ml of hydrocarbon with an equal volume of bromine solution in a dry test tube, and divide the mixture into four approximately equal portions. Add catalysts to three of them: a few crystals of iodine into one test tube, a piece of aluminium into the second, and a small quantity (a pinch) of iron filings into the third test tube. No catalyst is added to the fourth portion.

Keep the mixtures containing toluene at room temperature and jolt them at short intervals. Heat the mixtures containing benzene to boiling (better on a water bath) and then place in the stand.

Observe the different rates and intensities of evolution of hydrogen bromide (cf. Experiment 148), and note which hydrocarbon is brominated faster. Assess the catalytic action of the added substances.

B. In order to establish the effect of the catalyst not only on the rate but also on the direction of toluene bromination, heat the mixtures to boiling with and without iron. The bromination is energetic in both cases. Cool the test tubes and dip the end of a filter paper strip twisted into a wick to wet the paper. Remove the papers, slight-

y dry them over a hotplate, or simply in the air, and feel (CAREFULLY!) the odour of the wet end from time to time. Hydrogen bromide and the solvent are volatilized very quickly; then toluene, taken in excess, is evaporated. Now the markedly different odours of the papers can be estimated.

At the end of the experiment, rinse all test tubes with warm alkali solution in the hood.

150
Effect of Light on Bromination of Aromatic Hydrocarbons

REAGENTS

Benzene.
Toluene.
Xylene.

Carry out the experiment in three narrow test tubes or thin-walled glass tubes sealed at one end. Place approximately equal volumes of hydrocarbons into the tubes. The height of the liquid column in the tube should be not less than 7-8 cm. Pull a piece of rubber tubing (or a black paper sleeve) on each test tube to protect not less than 3-4 cm of the liquid column from direct light.

Add 5-10 drops of bromine solution into each test tube, shake, and place them in scattered light, or illuminate by an electric lamp (60 W or over) from a distance of 2-3 cm. See to it that the luminous fluxes incident on the test tubes should be equal. Record the time when the experiment begins.

In 1-10 minutes (depending on thickness of the test tube walls and intensity of illumination) the visible portion of the liquid column is decolourized first in one and then in the other test tube. Note the time of decolouration of each solution. Remove the light-protecting tube (black paper) and see whether or not the bromine colouration has vanished in the part of the column protected from the action of light.

A fuming gas can be seen at the mouth of the test tube where the liquid is decolourized. Sometimes, gas bubbbes can be seen in the liquid. Dip strips of filter paper and smell the odour of the reaction products in the decolourized solutions after evaporation of more volatile substances (see the previous experiment).

The bromine colour persists in one solution for a very long time.

151
Preparing Bromobenzene

REAGENTS

Benzene.
Bromine.
Iron, coarse filings or pieces of a nail.

Use the HOOD.

Carry out the experiment in a test tube tightly stoppered with a plug through which a bent outlet tube is passed (Fig. 14). Connect a glass tube packed with granulated soda lime placed between two cotton wool pads. The adsorption tube should be inclined downwards. The length of the tube is 10-15 cm, the diameter about 1 cm.

Place 5 ml of benzene, 1 g of iron, and 2 ml of bromine into the test tube. Close it immediately and fix in the stand clamp. The reaction begins immediately and proceeds very smoothly. Gas bubbles are liberated, but the mixture almost does not get warm. The liberated hydrogen bromide is well absorbed by soda lime that becomes yellow and very hot. Drops of water that are formed in the absorption tube slip to the free end of the tube. Only a faint odour of benzene could be smelt at the exit from the absorption tube, provided the experiment procedure is strictly followed. In 10-15 minutes the bubbling discontinues and the colour of the bromine vapour over the liquid becomes almost invisible. Heat the test tube on a water bath at 60-70 °C for a few minutes, then cool the mixture in cold water, and dismantle the apparatus.

Transfer the red oil from pieces of iron into another test tube, shake with soda solution, then two times with water, transfer by a pipette (see Experiment 3) into a dry test tube, add 2-3 pieces of calcium chloride, and heat for a few minutes on a warm water bath until cloudiness disappears. Decant the coloured liquid into a test tube provided with an outlet tube and a thermometer, add a boiling stone, and distil with an air-cooled condenser. Collect separately the fractions boiling out at temperatures below 140 °C (mainly excess benzene) and at a temperature range from 140 to 160 °C.

Transfer the still bottoms onto a watch glass: dibromobenzene crystallizes on cooling. Remove excess liquid on a filter paper and re-crystallize, if necessary, from a small volume of alcohol.

Crystallization of dibromobenzene at room temperature shows which of its possible isomers is mainly formed in conditions of the given experiment.

Repeated distillation of the fraction boiling out at 140-160 °C gives a sufficiently pure bromobenzene, boiling within a range of temperatures from 152 to 156 °C. The yield is about 4 g.

Bromination (chlorination) of aromatic hydrocarbons is as a rule substitution of the halogen for one or several hydrogen atoms with liberation of hydrogen halide:

$$ArH + Br_2 \rightleftharpoons ArBr + HBr$$

The structure of the hydrocarbon and the conditions of the reaction produce a marked effect on the course of the reaction. In the absence of catalysts, the hydrogen atoms in benzene and in the aromatic nucleus of its homologues are not replaced by halogens even with boiling. Hydrogen atoms of the side chains (e.g. in the CH_3- group of toluene, especially in one CH_3- group of xylene) are quickly replaced by halogens. Toluene gives in these conditions benzyl bromide (b.p. 199 °C):

$$C_6H_5CH_3 + Br_2 \longrightarrow C_6H_5CH_2Br + HBr$$

and xylene gives xylyl bromide, $CH_3C_6H_4CH_2Br$ (b.p. 212 °C). These halogen-substituted compounds are characterized by irritating odour and lacrimating power.

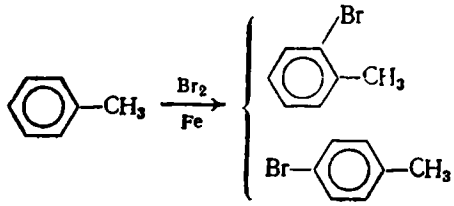
The substitution of the first halogen atom into the side chain of aromatic hydrocarbon occurs faster than its further halogenation.

Under the action of direct sun rays, chlorine and bromine do not replace the hydrogen atom in benzene by the halogen, but three halogen molecules are added across the aromatic bonds of the benzene nucleus to give hexachloro- or hexabromocyclo-hexane. In conditions of the experiment the reaction is very slow. If the molecules of bromine are activated by heating or illumination, the reaction becomes a radical-chain one (see explanations to Experiment 18).

Iron and aluminium react with bromine to give the bromides $FeBr_3$ and $AlBr_3$, which are catalysts in these reactions. During bromination of benzene or its homologues in the presence of such catalysts, the latter polarize the bromine molecule and then bind the bromide anion to give a complex anion. The other bromine atom accepts the positive charge and attacks the aromatic nucleus of hydrocarbon as an electrophilic agent. First it forms a complex with hydrocarbon, then draws off a pair of electrons from the benzene nucleus and adds to it, while the hydrogen ion adds to the other, negative bromide ion of the complex anion. The reaction here is the electrophilic substitution type.

Various chemical catalysts (iodine, iron, aluminium) not only activate halogens to form their compounds, but also direct their action for substituting the halogens for the hydrogen atoms of the benzene nucleus. This directed action of the catalysts is so energetic that toluene, for example, in the presence of iron, is brominated, even at high temperature and illumination, to give a mixture only

of *o*-bromotoluene (b.p. 182 °C) and *p*-bromotoluene (m.p. 28 °C, b.p. 184 °C):



Products of further bromination of the nucleus are formed in the presence of excess bromine. Unlike hydrocarbon derivatives having halogens in their lateral chain (see Experiments 149, 150) all these compounds with the nucleus-substituted halogen have no pungent odour or lacrimating action.

In the presence of catalysts, benzene is quickly brominated to give bromobenzene, C_6H_5Br (b.p. 156 °C), and a mixture of isomers of dibromobenzene (with prevalence of the para-isomer). The melting point of *o*-dibromobenzene is 6 °C, of *m*-dibromobenzene —7 °C, and of *p*-dibromobenzene, 87 °C. The reaction is more quiet if benzene is taken in excess (see Experiment 151), and the yield of bromobenzene is higher, since the formation of dibromobenzene and resinous products decreases in these conditions. In Experiment 149, A, benzene, even in the presence of catalytic metals and with heating, is brominated slower than toluene at room temperature (with catalysts). The difference in the reaction rates is easy to estimate by the intensity of liberation of hydrogen bromide.

Naphthalene, whose molecule is two condensed benzene rings, is brominated easier than benzene, to give 1-bromonaphthalene (b.p. 280 °C).

152
Bromination of Styrene (Preparing (1.2-Dibromoethyl) benzene)

REAGENTS

Styrene (see Experiment 264).

Bromine, approximately 3-5 per cent solution in glacial acetic acid.

Place 5-6 drops of styrene into a test tube and add, in small portions with shaking, bromine solution until its colour persists. Dilute the obtained pale yellow liquid with two volumes of cold water, and in 5-10 minutes separate the white precipitate on a filter with suction (see Fig. 6).

The obtained dibromide can be recrystallized from ethyl alcohol by adding water (see Experiment 2). The melting point of the product is 71 °C.

The bromination reaction occurs only across the side chain of the styrene molecule (cf. Experiments 148-151). The hydrogen atoms are not replaced by bromine. The reaction is the electrophilic addition type (see explanations to Experiment 18). It is fast and quantitative. The reaction is used in industry for iodimetric determination of styrene in the reaction mixture (manufacture of styrene from ethylbenzene by catalytic dehydrogenation).

If bromine solution in acetic acid is used (rather than in carbon tetrachloride or chloroform, as is the case with Experiments 148-150), the precipitation of an insoluble reaction product is facilitated, since unlike the halogen-substituted hydrocarbons, acetic acid is miscible with water.

153
Mobility of Halogen in Various Halogen-Substituted Aromatic Hydrocarbons

REAGENTS

Chlorobenzene, or *bromobenzene*.
Benzyl chloride, or *(1,2-dibromoethyl)benzene* (see Experiment 152).
Silver nitrate, saturated alcoholic solution (see Experiment 32).

Dissolve (1,2-dibromoethyl)benzene in a small volume of ethyl alcohol.

Use a few drops of each test liquid in the reaction of elimination of halogen, first by the action of alkali (see Experiment 31), and then by the action of alcoholic silver nitrate (see Experiment 32). The difference in mobility of halogen, depending on its position in the molecule, is quite vivid in both experiments.

Test the original chlorides and bromides by washing with water for the presence of halogen that can be ionized (see Experiment 31). Decompose benzyl chloride residues by alkali.

The strength of halogen bond in halogen-substituted aromatic hydrocarbons strongly depends on their structure. The halogen-carbon bond in them is markedly less polar than in halogen derivatives of alkanes. Therefore, the halogen-bonded carbon of the aromatic nucleus is less positive; it is less susceptible to the attack of nucleophilic agents, and the atom of halogen bonded with the carbon atom of the benzene nucleus fails to be eliminated either by alkali (aqueous or alcoholic), or by alcoholic solution of silver nitrate.

The low reactivity of halogen makes halogen derivatives of this type (e.g. chlorobenzene) similar to the fatty compounds in which halogen is attached to the atom of carbon double-bonded with another carbon atom, e.g. vinyl chloride, $CH_2=CHCl$.

In some other reactions (e.g. with magnesium in ether, and with sodium metal) the atom of halogen attached to the atom of a ring carbon is quite mobile. In aromatic hydrocarbons with halogen substituted in the α-position (to the ring) in the side chain, the halogen is eliminated (for example, by hydrolysis) easier than in most halogen-substituted alkanes.

These reactions of nucleophilic substitution of the S_N1 type begin with ionization of the α-halogen derivative with subsequent bonding of the nucleophile by the carbonium cation. The hydrolysis of the α-halogen derivatives in some solvents is the S_N2 reaction (see explanations to Experiment 27).

154
Oxidability of Aromatic Hydrocarbons

REAGENTS

Benzene.
Toluene.

Carry out simultaneously experiments with benzene and toluene. Place 1 ml of potassium permanganate and 1 ml of dilute sulphuric acid into each of the two test tubes and add a few drops (about 0.5 ml) of benzene into one and the same amount of toluene into the other test tube. Strongly shake both for a few minutes. The colour of the mixture quickly changes in one test tube, the change being especially marked at the interface between the hydrocarbon drops and the aqueous layer. The colour of the mixture in the other test tube almost does not change.

Benzene is quite stable to oxidants and practically does not react with potassium permanganate, either in acid or in alkaline medium. Commercial benzene sometimes contains toluene admixtures and gives a vivid reaction with potassium permanganate on heating. Benzene homologues are oxidized comparatively easily (see explanations to Experiments 182 and 183).

155
Sulphonation of Aromatic Hydrocarbons

REAGENTS

Benzene.
Toluene.
Xylene.
Naphthalene.

Place 0.5-1 ml (0.5-1 g for naphthalene) of each hydrocarbon into separate test tubes and add 4 ml of concentrated sulphuric acid into each. Heat the test tubes to 80 °C on a water bath with strongly shaking at short intervals. Naphthalene first partly solidifies on the walls of the test tube above the liquid level, and it should be melted by carefully heating the deposited substance. Heat the test tube containing benzene with greater care so that benzene does not evaporate.

Hydrocarbons form emulsion on shaking with the acid (the longer the process, the easier) and gradually dissolve. Note the difference in time taken to dissolve the test hydrocarbons.

When the dissolution is completed, cool the test tubes in water in a beaker, then transfer the contents of each test tube into a flask or a beaker containing 10-15 ml of cold water, and note whether the original hydrocarbon or the reaction product precipitates.

Unlike saturated fatty hydrocarbons (see Experiment 20), aromatic hydrocarbons react with sulphuric acid to give sulphonic acids according to the general equation:

$$Ar\text{—}H + HO\text{—}SO_2OH \longrightarrow H_2O + ArSO_2OH$$

This reversible reaction is electrophilic substitution. The nature of the electrophilic group of atoms formed from the molecule of sulphuric acid is disputable.

Xylene is the fastest of the taken hydrocarbons to be sulphonated and dissolved (in 5-10 minutes). Toluene and naphthalene are sulphonated much slower, and benzene is the slowest of all. Sulpho groups are attached to toluene and xylene molecules mostly in the ortho- and para position with respect to the CH_3 groups, and to naphthalene molecule, at temperatures below 100 °C, only in the 1 (α) position. Unlike the original hydrocarbons, the formed sulphonic acids are quite strong. The acids and their salts with alkali and alkaline earth metals are readily soluble in water.

The introduction of the sulpho group is often used to increase solubility of some substances, for instance, dyes (see Experiment 244).

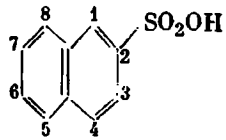
156
Preparing β-Naphthalenesulphonic Acid

REAGENTS

Naphthalene.

Place about 1 g of naphthalene in a dry test tube and melt it. Cool the melt and add an equal volume (about 1 ml) of concentrated sulphuric acid. Heat the mixture very carefully over a burner for 1-2 minutes with shaking until a homogeneous liquid mixture is obtained. Cool it and add 2 ml of water to the thick dark mass. Slightly heat the test tube contents again. When the mixture is then cooled to 15-20 °C, β-naphthalenesulphonic acid precipitates. It can be separated on a funnel with a disk and dried. If to the mixture with crystals another portion (3-5 ml) of water is added, the acid is fully dissolved.

In our experiment naphthalene is sulphonated at a temperature of 150-180 °C, and unlike in the previous experiment, gives almost exclusively beta-naphthalenesulphonic acid



since the sulpho group of α-sulphonic acid is easily eliminated in the form of sulphuric acid by the electrophilic attack of the hydrogen ion on the α-carbon atom. The β-carbon atom of the naphthalene molecule is less nucleophilic and beta-sulphonic acid is more stable at the temperature of the experiment. It is less soluble in water than the alpha-isomer, and is crystallized with three molecules of water. The crystal trihydrate melts at 83 °C. The monohydrate melts at 124 °C, and anhydrous acid at 91 °C.

157
Reaction of Aromatic Hydrocarbons with Concentrated Nitric Acid

REAGENTS

Benzene.
Toluene.
Xylene.

Use the HOOD.

Carry out simultaneously the test with all the three substances.

Place 2-ml portions of concentrated nitric acid into three separate test tubes and add 5-7 drops of each hydrocarbon. Shake strongly:

an unstable, quickly segregating emulsion is formed in the test tubes. Heat the mixtures almost to boiling with shaking at short intervals. Observe the difference in reactions. The emulsions gradually become more stable in all of them.

Heat with shaking for 5-10 minutes, cool the test tubes, and add 6-7 ml of cold water into each. Note the characteristic odour of the reaction products. In two test tubes it is a heavy coloured oil.

Concentrated nitric acid nitrates aromatic hydrocarbons and simultaneously oxidizes their side chains to liberate nitrogen oxides (cf. Experiments 22, 182 and 183). In our experiment the reaction is the fastest and most energetic with xylene, and the slowest with benzene (cf. Experiment 158). Many mononitro derivatives, having the density over unity, are formed in the test tubes containing toluene and xylene. The aromatic mononitro compounds are characterized by the specific odour of almonds (see also Experiments 158-161 and explanations to them).

158
Preparing Nitrobenzene

REAGENTS

Benzene.

Prepare a nitrating agent by mixing, in a wide test tube or a small flask, 1.5 ml of concentrated nitric acid with 2 ml of concentrated sulphuric acid, and cooling the hot mixture. Add, drop by drop, 1 ml of benzene with strongly but carefully shaking. The reaction is highly exothermic, and the mixture should therefore be cooled in water. Shake the test tube constantly to emulsify the upper layer in the lower layer of the mixture. In 3-5 minutes, transfer the reaction mixture into a beaker containing 20-30 ml of water, shake, and allow to stand. Nitrobenzene is separated in the form of a heavy yellowish oil, clouded with drops of water.

The obtained nitrobenzene can be used for further nitration (Experiment 159).

If pure nitrobenzene is required, transfer it by a pipette into a test tube containing pure water and shake the mixture. Separate nitrobenzene, transfer it into a small dry test tube, and dry with a piece of fused calcium chloride with heating on a water bath until the solution becomes clear. Only traces of the original benzene remain in nitrobenzene. They can be removed by distillation.

The yield of nitrobenzene is about 70 per cent.

159
Preparing Dinitrobenzene

REAGENTS

Nitrobenzene (reagent prepared in Experiment 158 can be used).

Use the HOOD.

Prepare a nitrating mixture of the same composition as in the previous experiment using 1.5 ml of nitric acid and 2 ml of sulphuric acid. Place about 1 ml of nitrobenzene into the hot acid mixture and heat for 15 minutes on a boiling water bath with frequently and strongly shaking to emulsify the upper layer. Cool the reaction mixture and transfer it into four volumes of cold water: dinitrobenzene is separated in the form of a heavy oil that rapidly crystallizes. Many crystals of dinitrobenzene soon appear in the aqueous layer as well. The beautiful crystals are coloured yellow by impurities.

Separate the crystals on a filter with suction (see Experiment 1), wash on the filter with water, and dry on filter paper. The yield is about 70 per cent.

Place part of the obtained product into a dry test tube and lower it into a beaker with water. Heat the water on a gauze over a burner or on a hotplate. Measure the temperature of water at the moment when the crystals begin melting, and establish by this temperature which isomer of dinitrobenzene is obtained in the experiment.

Pure dinitrobenzene, re-crystallized from ethyl alcohol, is colourless.

Aromatic hydrocarbons and most of their derivatives can react with nitric acid to form nitro compounds. In this reaction the nitro group NO_2 replaces hydrogen at the carbon atom of the aromatic ring (see Experiment 157). Nitration of benzene is the electrophilic substitution reaction:

The easiness with which substances are nitrated varies, and either dilute or concentrated nitric acid is therefore used. To facilitate the nitration, a mixture of concentrated nitric and sulphuric acids (the nitrating mixture) is often used or a solution of a nitrate in sulphuric acid. Nitronium cation is formed in this mixture:

$$HONO_2 + H_2SO_4 \rightleftharpoons H_2O + HOSO_2ONO_2 \rightleftharpoons H_2O + HOSO_2O^- + NO_2^+$$

which is the electrophilic nitrating agent.

If the proportion of the nitrating mixture or nitric acid increases, and also if the reaction temperature is raised, a second, and some-

times even a third nitro group can be introduced in the aromatic ring. The new nitro group is attached mainly in the meta position with respect to the existing nitro group. The yield of the ortho isomer is low, and only traces of the para isomer are produced.

When nitro groups are entered in the aromatic compound molecules the density of the new substance increases, and its boiling point rises. Nitro derivatives of aromatic hydrocarbons are insoluble in water and neutral. Some are coloured yellow.

The melting point of *o*-dinitrobenzene is 117 °C, of *m*-dinitrobenzene 90 °C, and of *p*-dinitrobenzene, 174 °C.

Reduction is the most important reaction of the nitro compounds (see Chapter 15, and also explanations to Experiment 22).

Prolonged inhalation of nitrobenzene and dinitrobenzene vapours, and also their uptake through skin, can produce headache. If the skin gets contaminated with nitrobenzene or dinitrobenzene, wash them out with water and soap immediately and then treat the skin with alcohol (see also Chapter 2).

160
Nitration of Toluene

REAGENTS

Toluene.

A. To attach one nitro group to a benzene ring, prepare the nitrating mixture out of 1.5 ml of concentrated nitric acid and 2 ml of concentrated sulphuric acid, and add, drop by drop, 1 ml of toluene with effectively cooling and shaking the mixture. Then proceed as instructed for nitration of benzene (Experiment 158).

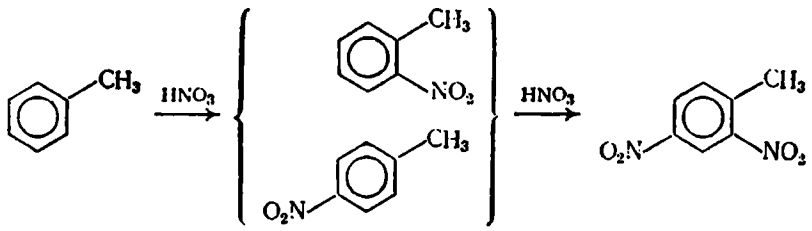
The oily product of nitration of toluene, which is isolated after pouring the reaction mixture into water, is a mixture of nitrotoluene isomers.

B. If another nitro group is to be attached to the benzene ring, prepare the nitrating mixture of the same composition and add the mixture of nitrotoluenes obtained in A to it. All further operations should be carried out in the same manner as in preparing dinitrobenzene (see Experiment 159).

Benzene homologues are usually nitrated easier than benzene itself. Nitration of toluene gives a mixture of *o*-nitrotoluene (b.p. 222 °C) and *p*-nitrotoluene (m.p. 54 °C, b.p. 238 °C). Very small quantities of the meta isomer are produced in these conditions.

When the mixture is further nitrated, and the second nitro group is entered in the ring in the meta position with regard to the already

attached group. both nitrotoluene isomers convert mainly into 2,4-dinitrotoluene



The melting point of this dinitrotoluene isomer, isolated from the water-acid solution in test B, is 70 °C.

Bromobenzene can be nitrated in the same way as toluene (but without cooling). para-Nitrobromobenzene, melting at 126 °C, is predominantly formed in this case.

M. I. Konovalov showed (1888-1893) that at high temperature and with dilute nitric acid, it is possible to introduce the nitro group not into the benzene ring but into the lateral chain of the aromatic hydrocarbon, and even into molecules of other type hydrocarbons. The reaction mechanism is radical (see explanations to Experiment 22). Toluene in these conditions gives phenylnitromethane, $C_6H_5CH_2NO_2$, which forms in small quantities during common nitration of toluene as well.

161
Preparing Nitronaphthalene

REAGENTS

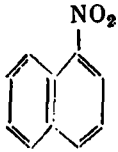
Naphthalene, powder.

Place 2 ml of concentrated nitric acid in a test tube and add 0.5 g of naphthalene. Shake the mixture: yellow colouration develops at room temperature. Heat the mixture on a boiling water bath for 5 minutes with shaking at short intervals and then pour into four volumes of cold water.

Nitronaphthalene is separated as an orange oil that quickly solidifies on shaking. The yield is close to theory. The product can be purified by re-crystallization from a mixture of alcohol and water (see Experiment 2).

Naphthalene is nitrated easier than benzene or toluene. Nitric acid alone can therefore be used instead of the nitrating mixture.

In our experiment, the reaction product is mostly alpha-nitronaphthalene (m.p. 61 °C)



containing a small amount of 1,5-dinitronaphthalene.

162
Condensation of Aromatic Hydrocarbons with Halogen Derivatives in the Presence of Aluminium Chloride

REAGENTS

Benzene.
Chloroform.
Aluminium chloride, anhydrous powder.

Use the HOOD.

Place 1 ml of benzene in a dry test tube, add a small amount (0.2-0.3 g) of aluminium chloride, and finally 0.5 ml of chloroform. If the mixture is now slightly heated (sometimes at room temperature) an energetic reaction begins. It is accompanied by liberation of heat and evolution of ample quantities of hydrogen chloride, strongly fuming in the air. The powder of aluminium chloride turns into a thick coloured oil.

One of the most characteristic reactions of aromatic hydrocarbons is their ability to condensation with halogen-substituted hydrocarbons and acid halides in the presence of a special catalyst, anhydrous aluminium chloride. Hydrogen halide is eliminated in this reaction to form a new carbon-carbon bond with participation of a carbon atom of the benzene ring. The reaction between benzene and chloroform gives mostly triphenylmethane according to the equation:

$$3C_6H_6 + CHCl_3 \longrightarrow CH(C_6H_5)_3 + 3HCl$$

Acid chlorides are condensed with aromatic hydrocarbons to give ketones in these conditions:

$$ArH + ClCOR \longrightarrow ArCOR + HCl$$

Aluminium chloride reacts with the original substances, and sometimes with the end products of the reaction, to give complex compounds, which are usually oil-like substances. To isolate the end products from these complex compounds, the latter should be decom-

posed with hydrochloric acid. The method was developed by Friedel and Crafts in 1877, but aluminium chloride was first used as a catalyst in organic chemistry by Gustavson in the seventies of the past century in Moscow.

Alkylation of a benzene ring is the reaction of electrophilic substitution. Being part of a complex with $AlCl_3$, the halogen derivative gives off the halide ion as the fourth ligand to form carbonium cation with the positively charged carbon atom. This cation reacts with the benzene ring as an electrophile to replace hydrogen and to give it its own charge. Complexes with $AlCl_3$ are coloured. Benzene and its homologues produce orange or red complexes of various shades, naphthalene produces blue, and anthracene green complexes.

Condensation in the presence of anhydrous aluminium chloride is of great preparative importance, but it is often complicated by side processes.

Aluminium chloride can sometimes be replaced by anhydrous ferric chloride and other halides.

163
Formation and Decomposition of Naphthalene Picrate

REAGENTS

Naphthalene.
Picric acid.
Ethyl alcohol.

A. Place a few crystals of naphthalene into a test tube, and about the same quantity of picric acid into another. Add 1 ml of alcohol to both and shake the test tubes for a few minutes. Allow the liquids to stand, decant the clear saturated solutions thus obtained, and mix their approximately equal volumes in a separate dry test tube.

Yellow crystals of naphthalene picrate abundantly precipitate in a few minutes.

B. Separate the obtained picrate on a funnel with suction and wash with a few drops of alcohol. Transfer the crystals into a test tube containing 3-5 ml of water. Add 1 ml of concentrated ammonia solution and heat the mixture on a hot water bath (50-60 °C), with shaking at short intervals. The needles of the picrate disappear, and grains of naphthalene precipitate. The aqueous solution turns yellow. The obtained naphthalene has the specific odour.

In 5-10 minutes, transfer the liquid together with the precipitate onto a round piece of clean paper wetted with water and placed on the disc in the same funnel. Suck off the yellow liquid and wash the precipitate with water containing a little of ammonia. Pure, almost colourless naphthalene is thus obtained.

Picric acid (see Experiment 173) reacts with many aromatic hydrocarbons, phenols, amines, ethers, aldehydes, and aromatic ketones, and also with various heterocyclic compounds to give readily crystallizing molecular complexes. Some of them, for example, benzene picrate, are unstable, but others, especially picrates of polynuclear hydrocarbons, are more stable. The number of attached molecules of picric acid is usually equal to the number of benzene rings of the hydrocarbon (assuming the condensed system to be one ring). Thus, triphenyl-methane attaches three molecules of picric acid, diphenylethane (dibenzyl) two, and benzene, naphthalene, anthracene, and phenanthrene only one molecule. Naphthalene picrate, $C_{10}H_8 \cdot C_6H_2(NO_2)_3OH$, melts at 149 °C and only slightly dissolves in water and alcohol. Its formation is used in quantitative determination of naphthalene. When heated in excess alcohol, the picrate falls into its constituent parts.

When heated, hydrocarbon picrates are easily split by aqueous ammonia into the original hydrocarbon and a readily soluble ammonium picrate.

Picrates of hydrocarbons were first prepared and studied by Fritzsche in Russia. By now they are known as 'charge transfer complexes', in which the molecule of picric acid joins partly or completely with one of the π-electrons of the molecule of aromatic hydrocarbon. Not only picric acid, but other compounds as well, for instance trinitrobenzene, can form such charge transfer complexes.

CHAPTER THIRTEEN

PHENOLS AND NAPHTHOLS

Substances used in the experiments of this chapter are given in Table 11.

Nitrophenols should be prepared during the experiments (Experiment 172).

If picric acid is not available, mix 2 g of phenol and 2.5 ml of concentrated sulphuric acid in a test tube with gently heating, and add the obtained liquid to 8 ml of concentrated nitric acid (use the HOOD). Boil the mixture in a beaker on a gauze over a burner to reduce its volume two times. Now add 8 ml of nitric acid again and continue boiling. When the brown oil, which first separates, disappears, transfer the clear liquid into 100 ml of cold water. In 30-40 minutes separate the precipitated crystals of picric acid on a filter with suction and press out excess liquid. Picric acid can be re-crystallized from 50 per cent alcohol.

Picric acid is sparingly soluble in water (1.4 g in 100 g at 20 °C and 8 g at 100 °C), ethyl ether, and chloroform. The acid better dissolves in ethyl alcohol and hydrocarbons. It dissolves well in acetone.

164
Solubility and Acid Character of Phenols and Naphthols

REAGENTS

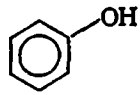
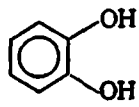
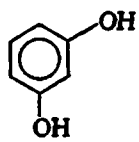
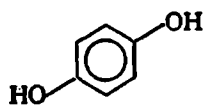
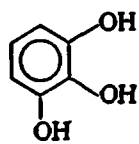
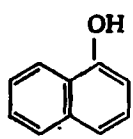
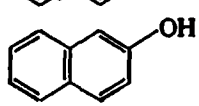
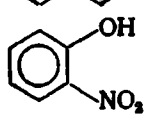
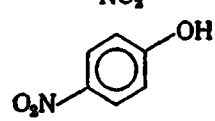
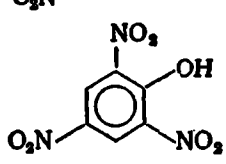
Phenols (*carbolic acid*, *pyrocatechol*, *resorcinol*, *hydroquinone*, *pyrogallol*, *alpha-* and *beta-naphthols*).

Carry out simultaneously several experiments with different substances.

Place 0.3-0.5 g of a phenol into a test tube and add 4-5 ml of water. Shake the mixture: if the substance does not dissolve completely.

Table 11

Melting and Boiling Points of Phenols and Naphthols

Substance	Formula	M. p., °C	B. p., °C
Phenol		41	182
Pyrocatechol		105	240
Resorcinol		110	277
Hydroquinone		170	286
Pyrogallol		132	309
α-Naphthol		96	280
β-Naphthol		122	286
o-Nitrophenol		45	215
p-Nitrophenol		114	279 (with decomposition)
Picric acid		122	Sublimes, explodes

heat the mixture to boiling, then cool, and observe the changes. Try the reaction of the obtained solution to litmus: place a drop of each solution onto a blue test paper.

Aqueous solutions of phenols are used in further experiments.

The simplest phenol, carbolic acid, C_6H_5OH, is only moderately soluble in water at room temperature: 6 g per 100 ml. At the same time, excess phenol dissolves water and its melting point sharply decreases, since the cryoscopic constant of phenol is very high: 7.4 (cf. Experiments 8 and 12). Two liquid layers are formed as a result, namely, solution of phenol in water, and oil-like solution of water in phenol. The mutual solubility of water and phenol increases with heating. At temperatures above 68 °C (critical temperature of mixing) phenol and water are miscible in all proportions.

The solubility of phenols in water increases with the number of hydroxyl groups, but the gradient is not regular throughout and depends on the mutual position of the hydroxyls in the benzene ring. Pyrogallol, and especially resorcinol are very well soluble. Hydroquinone's solubility is somewhat worse than that of phenol. Naphthols are sparingly soluble in cold and better in hot water. All phenols and naphthols are soluble in ethyl alcohol and ethyl ether.

Unlike alcohols, phenols give acid solutions provided their concentration is not too low. This is explained by protonization of the hydroxyl hydrogen under the effect of the aromatic nucleus that slightly draws the electrons of the oxygen atom. The acid character is especially marked in pyrogallol (pyrogallic acid), pyrocatechol, and naphthols. But naphthols are very sparingly soluble in water and their solutions give indistinct reaction to litmus.

The effect of the aromatic benzene ring on the ionization of the hydroxyl hydrogen increases if halogens or nitro groups are introduced into the ring (cf. Experiment 173).

165
Formation and Decomposition of Phenolates

REAGENTS

Phenol, crystals.
α- or β-*Naphthol*.

Carry out simultaneously two tests, with phenol and naphthol.

A. Place 0.3-0.5 g of a substance in a test tube and add 1 ml of water and dilute alkali solution to dissolve the original substance. Acidify the obtained clear solutions with dilute sulphuric acid: the original substance precipitates.

B. Place 0.2-0.3 g of phenol into two separate test tubes, and add with shaking 1-2 ml of sodium carbonate into one test tube and of sodium bicarbonate into the other. Phenol dissolves completely only in the solution of the carbonate to give phenolate.

Being acid, phenols react with caustic alkalis or their carbonates to give stable salt-like phenolates. For the simplest phenol, C_6H_5OH, the reaction is as follows:

$$C_6H_5OH + NaOH \rightleftharpoons C_6H_5ONa + H_2O$$

or, in the ionic form,

$$C_6H_5OH + OH^- \rightleftharpoons C_6H_5O^- + H_2O$$

Phenolates are usually well soluble in water and, unlike alcoholates, are not decomposed by water, although their solutions are strongly alkaline because of partial hydrolysis. Acids react with phenolate solutions to liberate free phenol:

$$C_6H_5O^- + H^+ \longrightarrow C_6H_5OH$$

The acid character of naphthol is more marked in this experiment than in the test with litmus (see Experiment 164).

Carbonic acid is ionized more strongly than phenol (see Experiment 75), and can displace it from phenolate solution. For the same reason phenol is sparingly soluble in bicarbonate solutions, whereas the carbonate solution contains many hydroxyl ions (the result of the hydrolysis) and therefore dissolves phenol well.

166
Bromination of Phenol in Anhydrous Medium

REAGENTS

Phenol, crystals.

Place a few crystals of phenol in a dry test tube and add 0.5 ml of bromine solution: the solution is decolourized immediately at room temperature, and hydrogen bromide is liberated in ample quantities.

As a result of incorporation of the hydroxyl group into the benzene ring, partial negative charges (—δ) arise at the second, fourth, and sixth carbon atoms of the ring (ortho and para positions), and the attack of the electrophilic agents on these carbon atoms is mar-

kedly facilitated. Bromination of phenols is the electrophilic substitution reaction. Compared with benzene and toluene (cf. Experiment 148), phenol is chlorinated and brominated much faster, and the reaction occurs at room temperature.

167
Action of Bromine on Phenols in Aqueous Solution

REAGENTS

Phenols, aqueous solutions (see Experiment 164).
Benzene.

Carry out simultaneously several tests with various phenols and naphthols.

A. Place 1 ml of each aqueous solution into separate test tubes and add 2 ml of bromine water. Observe the reaction.

Solutions of pyrocatechol, resorcinol, and pyrogallol change their colour. Hydroquinone solution first turns red, and then a dark green precipitate falls out. White and yellowish precipitates fall out from phenol and naphthol solutions.

B. Place 1 ml of aqueous solution of phenol, C_6H_5OH, in a test tube and add, drop by drop, bromine water.

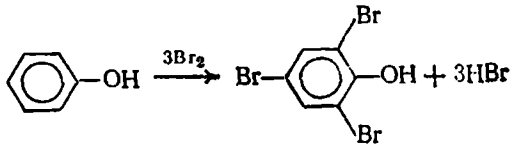
Cloudiness develops in solution. Shake the test tube: the solution becomes clear again. As bromine is further added (3-4 ml of bromine water), ample white precipitate falls out. The reaction product, tribromophenol, has a specific odour. Continue adding bromine water with shaking until the white precipitate turns pale yellow.

Heat the obtained mixture and boil in the HOOD for 1-2 minutes to remove excess free bromine. Cool the reaction mixture: the precipitate that was dissolved by heating falls out again. Add a few drops of potassium iodide solution and 1 ml of benzene to the cooled mixture, and shake strongly: the precipitate dissolves in benzene, and its layer is coloured violet by the liberated iodine.

Aqueous solutions of phenols react with bromine water to give various products that are different from products of bromination in an anhydrous medium (see Experiment 166). The difference is especially marked with hydroquinone, which is oxidized with bromine water to quinone that reacts with an excess of the original hydroquinone to give a sparingly soluble quinhydrone (see Experiments 225 and 226).

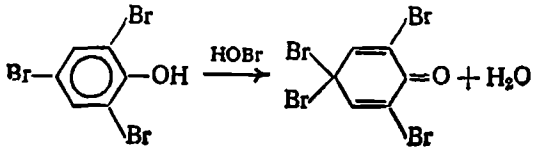
The products of reaction of resorcinol and pyrogallol with bromine water remain in solution. Naphthols in these conditions give precipitates of dibromosubstituted substances.

Bromination of phenol in aqueous solution is a fast process, and phenol is first quantitatively converted into a sparingly soluble (1 part by weight per 14,000 ml of water) colourless 2,4,6-tribromophenol (m.p. 96 °C):

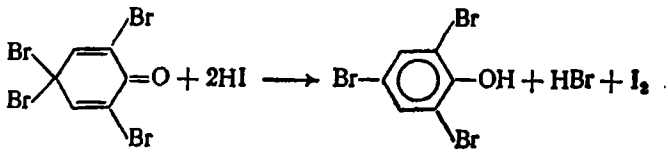


It can be re-crystallized from ethyl alcohol.

In the presence of excess bromine water, tribromophenol is brominated quantitatively to tetrabromophenol, which is 2,4,4,6-tetrabromocyclohexadienone:



This yellow product is sparingly soluble in cold water, well soluble in benzene. It reacts with potassium iodide in an acid medium (bromine water always reacts acid) to liberate iodine, and turns back into tribromophenol:



This reaction can be used for iodimetric titration of phenols in aqueous solutions.

168
Reaction of Phenols and Naphthols with Ferric Chloride

REAGENTS

Phenols, aqueous solutions (see Experiment 164).
Ethyl alcohol.
Potassium ferricyanide, 1 per cent solution.

A. Carry out simultaneously several tests with various phenols and naphthols.

Place 5-6 drops of each solution into separate test tubes and add 1-1.5 ml of water and a few drops (3-5) of ferric chloride solution.

Phenol and resorcinol solutions turn brightly violet, and pyrogallol solution turns brown red. Pyrocatechol solution first turns olive green, but when strongly diluted with water, its colour changes to violet blue. Hydroquinone solution first becomes green, then brown, and beautiful dark green needles of quinhydrone precipitate on standing. The solution of alpha-naphthol first reacts with ferric chloride to turn slightly green, but later white flakes quickly precipitate from the solution. They turn violet on standing. The precipitation from the beta-naphthol solution is a slower process.

B. Divide the coloured solutions containing phenol, resorcinol, and pyrogallol (obtained in test A) into three parts. Add an equal volume of alcohol to one part and a few drops of alkali solution to the other part. The added reagents destroy the original intense colour of the solutions.

C. Decant part of the supernatant liquid from the settled solutions containing hydroquinone and naphthols (test A) and add a few drops of potassium ferricyanide solution: a blue precipitate (Turnbull's blue) falls out.

Many phenols and more complicate compounds containing the phenol hydroxyl in their molecule react with ferric chloride in an aqueous, water-alcohol, or chloroform solution to give intense colouration characteristic of each particular phenol. The colour is due to the strongly ionized complex phenolates of tervalent iron, which are formed according to the equation:

$$FeCl_3 + 6ArOH \longrightarrow 6H^+ + 3Cl^- + [Fe(OAr)_6]^{3-}$$

Addition of acid, glycerol, alcohol, and sometimes excess ferric chloride, decreases the degree of phenolate dissociation (hence the concentration of coloured ions decreases), and the colour of the solution vanishes. Alkalizing also destroys the colour by binding the iron ion into its hydroxide.

Ferric chloride can also oxidize phenols. It oxidizes hydroquinone to quinone, which then gives quinhydrone (see Experiments 225 and 226). Naphthols are oxidized by ferric chloride to give sparingly soluble dinaphthols, in which two naphthalene rings are combined:

$$2C_{10}H_7OH + 2FeCl_3 \longrightarrow HOC_{10}H_6C_{10}H_6OH + 2FeCl_2 + 2HCl$$

Other phenols also form phenolates of iron with partial oxidation.

Acting as an oxidant, a ferric salt converts into a ferrous salt. This can easily be detected by the usual reagent for divalent iron, potassium ferricyanide:

$$3Fe^{2+} + 2[Fe(CN)_6]^{3-} \longrightarrow Fe_3[Fe(CN)_6]_2$$

169
Oxidability of Phenol and Naphthol

REAGENTS

Phenol and α- or β-naphthol, aqueous solutions (see Experiment 164).

Place 0.5-1 ml of an aqueous solution of phenol or naphthol into a test tube and add an equal volume of sodium carbonate solution. Now add, drop by drop and with shaking, potassium permanganate solution. In both cases the colour of potassium permanganate disappears and manganese dioxide precipitates very soon at room temperature.

As a rule phenols are oxidized simultaneously in different directions to give a complicate mixture of reaction products. Easier oxidability of phenols compared with aromatic hydrocarbons is explained by the effect of the hydroxyl group, which markedly increases the mobility of hydrogen atoms attached to other carbon atoms of the benzene ring because of the charge redistribution on the carbon atoms (see explanations to Experiment 166). Polyhydric phenols (especially those with the hydroxyl groups attached in the ortho and para positions) are oxidized with even greater easiness (see Experiment 170) and are very strong reductants. In alkaline solutions they easily reduce salts of silver and copper.

170
Oxidation of Pyrogallol with Atmospheric Oxygen

REAGENTS

Pyrogallol.

Place 0.3-0.4 g of pyrogallol and 2-3 ml of concentrated alkali solution into a test tube or a 20-25 ml bottle. Close the vessel tightly with a plug through which an outlet tube is passed, and lower the tube end to the bottom of another test tube containing 5-6 ml of stained water. Shake the mixture: water is sucked from the test tube into the outlet tube since the original volume of air in the reaction vessel decreases by about 20 per cent. The mixture of pyrogallol and alkali darkens.

Polyhydric phenols are oxidized so easily that even their aqueous solutions (see Experiment 164) are soon coloured on standing by the products of phenol oxidation by atmospheric oxygen. Oxidation of phenols in alkaline solutions is especially fast. Many phenols are

therefore used in photography as developers (hydroquinone, pyrogallol, etc.): they reduce salts of silver. Oxidation of pyrogallol in alkaline solutions is so energetic that oxygen is absorbed by this solution from air and other gaseous mixtures rapidly and quantitatively. This phenomenon is used in gas analysis. The reaction mechanism is very complicate, and hydrogen peroxide is formed in the reaction.

171
Sulphonation of Phenol and Naphthol

REAGENTS

Phenol.
β-Naphthol.

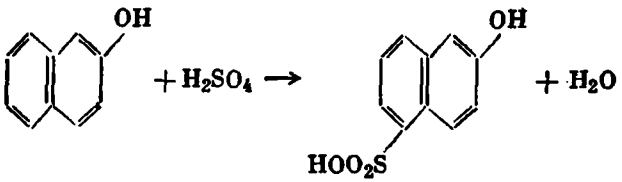
Place 2 g of a test substance and 3 ml of concentrated sulphuric acid in a test tube, and shake: the crystals of the original substance dissolve. But when 1 ml of water is added to a few drops of this solution (in a separate test tube), phenol and naphthol are precipitated as turbidity. Heat the main bulk of the reaction mixture on a boiling bath for 3-5 minutes, then cool, and carefully transfer the liquid into another test tube containing 10-12 ml of cold water.

A homogeneous solution is now formed, and the original substance does not precipitate. The solution containing phenol is almost fully devoid of the specific odour of phenol.

Sulphonation of phenols is the electrophilic substitution reaction (see Experiment 155) and its easiness is explained by the effect of the hydroxyl group on the distribution of charges in the benzene ring (see Experiment 166).

At room temperature, phenol gives mostly *o*-phenolsulphonic acid, and at 100 °C its para isomer.

In the conditions of our experiment, beta-naphthol gives 2-naphthol-6-sulphonic acid:



Other isomers of monosulphonic acids, and also disulphonic acids of phenol and naphthol are formed simultaneously, though in smaller quantities. The sulphonation products are soluble in water much better than the starting substances (cf. Experiment 155).

172
Preparing Nitrophenols and Their Properties

REAGENTS

Phenol, crystals.

A. Place 1 g of phenol into a test tube and add a few drops of water to prepare a homogeneous oily liquid (Experiment 164). Place 3 ml of concentrated nitric acid into another test tube and mix, with cooling, with 3 ml of water. Add the dilute (1 : 1) acid, in drops and very slowly, to phenol with strongly shaking and cooling the test tube. The reaction is vigorous. Transfer the reaction mixture into three volumes of water, shake, allow to settle, and pipette the separated heavy and dark oil first into a test tube containing water (for another washing), and then into a wide test tube fitted with an outlet tube. Fix the test tube in the inclined position in the stand, add 3 ml of water, drop a boiling stone, connect the tube and lower its other end into a clean receptacle.

Carefully heat the test tube over a burner, beginning with the upper layers and avoiding strong foaming. Distil about 1 ml of a cloudy liquid having the specific almond odour of *o*-nitrophenol. When the distillate is cooled, yellow low-melting crystals of *o*-nitrophenol precipitate. The product is very volatile. The yield is 0.2-0.3 g.

Decant the hot aqueous layer from the resinous still bottoms and cool it to 0 °C. Crystals of *p*-nitrophenol gradually precipitate. Separate them and dry.

B. Place a few drops of each saturated solution of nitrophenol in separate test tubes and mix with 1 ml of water. Then add, drop by drop, a dilute alkali solution and observe the colour change. Acidifying of the alkaline solution of nitrophenol with sulphuric acid restores the original colour.

C. Add a drop of ferric chloride solution to the aqueous solution of nitrophenol and observe whether or not the liquid is coloured as in the case with free phenol (see Experiment 168).

173
Properties of Trinitrophenol (Picric Acid)

REAGENTS

Picric acid, saturated solution.
White wool or silk (for test C).

A. Place 1-2 ml of saturated solution of picric acid into a test tube and add a few drops of dilute alkali. Note the change of colour and acidify with sulphuric acid.

B. Place 1-2 ml of picric acid into a test tube, add a drop of ferric chloride, and note the change of colour, if any.

C. Place 5-6 ml of saturated picric acid solution into a test tube and add wool or silk. Heat the contents on a boiling water bath with shaking at short intervals for 15-20 minutes. Decant the liquid and rinse the bright yellow fibres several times in water. Press out moisture and dry the fibres.

Phenols are nitrated much easier than aromatic hydrocarbons (cf. Experiment 157) and react vigorously even with dilute nitric acid.

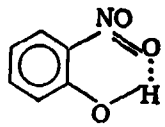
During nitration, the nitro group is attached to phenol mainly in the ortho and para position with regard to the phenol hydroxyl. Phenol, C_6H_5OH, first forms a mixture of 2- and 4-nitrophenols, with prevalence of the former (m.p. 45 and 114 °C respectively). Further nitration converts them into 2,4-dinitrophenol (m.p. 113 °C and finally into 2,4,6-trinitrophenol, i.e. picric acid. Other isomers of nitrophenol are obtained only in insignificant quantities.

Other processes occur simultaneously with nitration. These are oxidation of phenols with nitric acid, condensation, etc. As a result, dark coloured resinous side products, and also nitrogen oxides, are formed.

Introduction of nitro groups into the benzene ring strongly intensifies the acidic properties of phenols. The properties of nitrophenolates of alkali metals are very similar to those of true salts. Their solutions are bright yellow or orange red. The deeper colour of nitrophenols in alkaline solutions is explained by the changes in the structure of nitrophenol anion, as compared with its neutral molecule, and the quinonoid arrangement of the double bonds.

Unlike many phenols most nitrophenols do not give the specific colour reaction with ferric chloride.

o-Nitrophenol differs from *p*-nitrophenol by lower polarity and hence higher volatility, since the hydrogen atom of its hydroxyl group is additionally bonded by the hydrogen bond with the oxygen of nitro group:



These crab's claw-like forms, known as chelates or inner complexes, contain a new ring in the molecule and are produced by many compounds with adjacent OH and NO_2 (or CO) groups. In molecules of *p*- and *m*-nitrophenol these groups are at a greater distance from one another and the chelate is not formed. The molecules of these

isomers are therefore joined by hydrogen bonds with similar neighbouring molecules (associated); in aqueous solutions they are also bonded with water molecules (hydrated) and their volatility thus much decreases.

Picric acid gives fast colours to natural fibres (wool, silk), because it combines with free amino groups of proteins to form insoluble salt-like yellow products (Experiment 280).

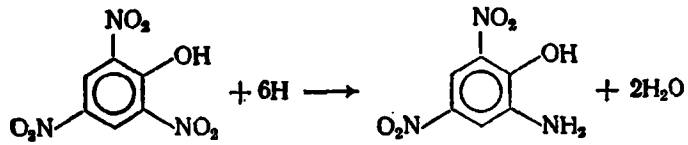
174
Reduction of Picric Acid

REAGENTS

Picric acid.
Glucose, powder.

Place a few crystals of picric acid in a test tube and add 3-4 ml of sodium carbonate solution and about 0.1-0.2 g of glucose. Boil the mixture for 2-3 minutes: the orange colour of sodium picrate turns gradually crimson red. Acidify the cooled liquid with dilute sulphuric acid: the red colour turns orange yellow.

Glucose, readily oxidized in alkaline solution (see Experiments 129-132) reduces one of the picric acid's nitro groups to amino group



Like other nitrophenols, the formed picramic acid (m.p. 169 °C) reacts with alkalis to give coloured salts (phenolates). The colour of alkaline solutions of picramic acid is very intense. Like picric acid, picramic acid also dyes natural fibres.

175
Nitroso Reaction of Phenols

REAGENTS

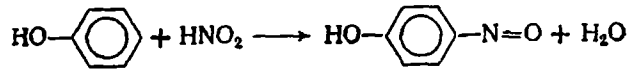
Phenol, saturated solution (see Experiment 164).
Potassium (sodium) nitrite, 0.1 per cent solution.

Place 0.5-1 ml of concentrated sulphuric acid into a test tube and add 2 drops of phenol solution (or a small crystal). Cool the obtained colourless solution and add a drop of the nitrite solution. Shake the

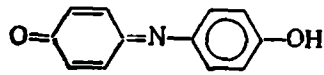
solution: it turns deep green. If the nitrite is added in excess, the colour turns violet blue or purple.

Transfer the intensely coloured liquid into another test tube containing 5 ml of water: a pink-red solution is formed. Add excess quantity of dilute alkali to 1 ml of this solution: the pink colour turns green and bluish. Acidify the solution: the pink colour is restored.

In conditions of our experiment, phenol first reacts with nitrous acid that is formed from the nitrite to give *p*-nitrosophenol (see Experiment 220 and explanations to it):



The product is readily condensed with excess phenol to give phenolindophenol having the quinonoid structure:



The latter reacts with acids and alkalis to give salts, in which the molecule of phenolindophenol turns into cation or anion respectively. These ions, whose structure is also quinonoid, colour the solution blue or green. When the acid solution is diluted with water, the solution is hydrolysed to liberate free red phenolindophenol (cf. Experiment 221).

Other substances that can eliminate nitrous acid, for instance, alkyl nitrites (see Experiment 54), can be used instead of the nitrite. Many phenols and their derivatives, having a non-substituted hydrogen atom in the ortho or para position with regard to one of the hydroxyl groups, give the colour reaction described above. The reaction was suggested by Lieberman.

p-Nitrosophenol is equilibrated in solution with its tautomeric form, *p*-benzoquinone monoxime (see Experiment 225).

176
Formation of Naphthol Picrates

REAGENTS

Alpha- and *beta-naphthols*, saturated solutions (see Experiment 164).

Picric acid, saturated solution.

Carry out simultaneously two experiments with both naphthol isomers.

Place 1 ml of naphthol solution into a test tube and add 1 ml of

picric acid. The orange α-naphthol picrate immediately precipitates. Yellow beta-naphthol picrate precipitates only gradually.

Like naphthalene (Experiment 163), naphthols react with picric acid to give sparingly soluble and well crystallizing molecular compounds, picrates, $C_{10}H_7OH \cdot C_6H_2(NO_2)_3OH$. The picrate of α-naphthol (m.p. 189 °C) is practically insoluble in water, and the picrate of β-naphthol (m.p. 156 °C) is soluble in water only in the quantity of 0.07 g in 1 litre.

The formation of picrates is used for quantitative determination of α- and β-naphthol in mixtures.

177
Preparing Ethers of β-Naphthol

REAGENTS

β-*Naphthol.*
Methyl iodide (see Experiment 28).
Ethyl iodide (see Experiment 29).
Sodium hydroxide, powder.
Ethyl alcohol.

A. Place 0.5 g of β-naphthol, 2.5 ml of dilute alkali solution, and 1 ml of methyl iodide into a test tube provided with a 'cold-finger' condenser. Carefully heat the mixture on a water bath, immersing in water first only the bottom of the test tube, and then (after appearance of an oil layer) the whole of it. In 20-25 minutes cool the mixture, add 10 ml of water, allow the precipitated oil to solidify, and separate the obtained product. The yield is about 0.4 g.

B. Place 0.5 g of β-naphthol, 2 ml of alcohol, 0.5 ml of ethyl iodide, and 0.2 g of solid sodium hydroxide in the apparatus as in test A. Heat the mixture for 20 minutes on a water bath, then remove the condenser, and heat the test tube in the flame of a burner to evaporate the greater part of the alcohol. Cool the mixture, add 10 ml of water, heat again until the molten oil floats to the surface, shake, cool in water, and separate the obtained crystals (see Experiment 1). The yield is about 0.4 g. Smell the odour of the obtained products.

Ethers of β-naphthol are formed by the S_N2 reaction, where the nucleophile is the naphtholate ion, $C_{10}H_7O^-$ (see explanations to Experiment 27).

Simple ethers of β-naphthol have a pleasant odour and are used in perfumery under trade names of Nerolin I (beta-naphthyl methyl ether, m.p. 72 °C, b.p. 274 °C) and Nerolin II, or Bromelia (beta-naphthyl ethyl ether, m.p. 37 °C, b.p. 282 °C). These compounds are quite stable to acids and alkalis and are distilled at high temperatures without decomposition. They are purified by re-crystallization from ethyl alcohol. It is difficult to purify beta-naphthyl methyl ether.

AROMATIC ALCOHOLS, ALDEHYDES, AND ACIDS AND THEIR DERIVATIVES

Compounds given in Table 12 are used in experiments of this Chapter.

Benzoic acid, phthalic acid, ethyl benzoate, dimethyl phthalate, and benzamide can be prepared during the experiment by the students (see Experiments 182, 183, 191, 192, and 197). The other recommended substances should be available in the laboratory ready for use.

178
Formation of Benzaldehyde Bisulphite

REAGENTS

Benzaldehyde.
Sodium bisulphite, saturated solution (see Experiment 70).

Place 0.5 ml of benzaldehyde and 2 ml of sodium bisulphite solution into a test tube and shake strongly. The odour of benzaldehyde soon disappears, and crystals of a new bisulphite precipitate. Shake again. If the volume of the precipitate does not increase any longer, add 6-8 ml of water and place the test tube in a water bath. The crystals soon disappear, the odour characteristic of benzaldehyde is felt, and oily drops appear in the solution.

The formation of bisulphite compounds of aldehydes and ketones was discussed earlier (see Experiments 70 and 71). Benzaldehyde

Table 12

Melting and Boiling Points of Aromatic Aldehydes and Acids and their Derivatives

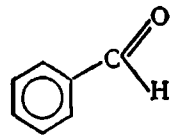
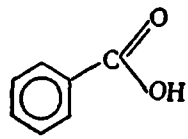
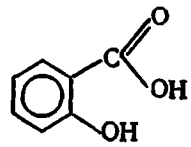
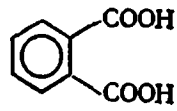
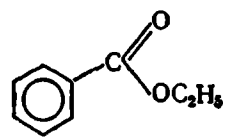
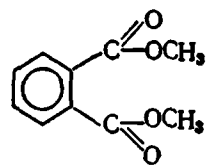
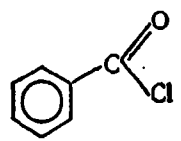
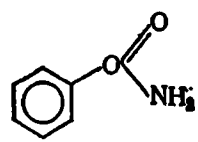
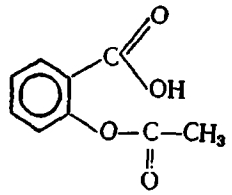
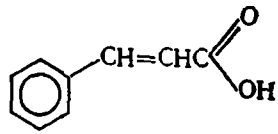
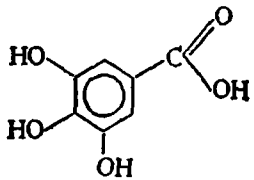
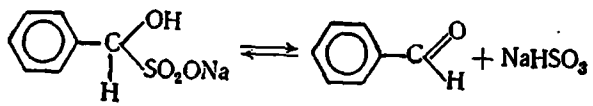
Substance	Formula	M. p., °C	B. p., °C
Benzaldehyde, density 1.05 g/cc		−26	179
Benzoic acid		122	250
Salicylic acid		159	Sublimes
Phthalic acid		~ 190 (decomposes)	—
Ethyl benzoate, density 1.05 g/cc		−34	213
Dimethyl phthalate, density 1.19 g/cc		—	282
Benzoyl chloride, density 1.21 g/cc		−1	198
Benzamide		130	290

Table 12 (continuation)

Substance	Formula	M. p., °C	B. p., °C
Acetylsalicylic acid		135	Decomposes
Cinnamic acid		133	300
Gallic acid		220 (decomposes)	Decomposes
Tannic acid	$C_{76}H_{52}O_{46}$	200 (decomposes)	—

bisulphite is decomposed by heating in an aqueous solution into the starting substances:



one of which is sparingly soluble in water.

179
Formation of Benzaldehyde Phenylhydrazone

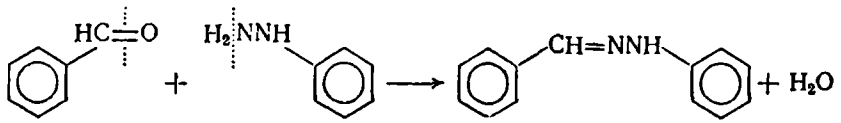
REAGENTS

Benzaldehyde.
Phenylhydrazine hydrochloride, crystals.
Sodium acetate.

Dissolve a few crystals (0.1-0.2 g) of phenylhydrazine hydrochloride and about 1.5 parts by weight of sodium acetate in 3-4 ml of

water. Add a few drops of benzaldehyde and shake: phenylhydrazone crystals precipitate.

The formation of phenylhydrazones, which usually well crystallize and have sharp melting points, is often used for identification of aldehydes and ketones (see Experiment 123). Phenylhydrazone of benzaldehyde is formed according to the equation:



Benzaldehyde phenylhydrazone (m.p. 156 °C) is very sparingly soluble in water.

180
Reaction of Benzaldehyde with Alkali (Cannizzaro-Tishchenko Reaction)

REAGENTS

Benzaldehyde.

Potassium hydroxide, about 10 per cent solution in alcohol (prepared for the experiment).

Potassium dichromate, powder.

To prepare alcoholic potassium hydroxide, mix 1 ml of concentrated potassium hydroxide solution (see Experiment 98) with 4 ml of ethyl alcohol (rectified).

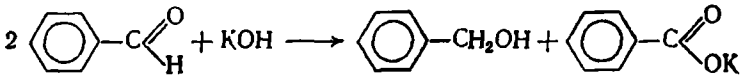
A. Place 1 ml of benzaldehyde into a test tube, add 5 ml of alcoholic potassium hydroxide, and shake. The mixture becomes hot and soon solidifies: ample quantities of potassium benzoate crystals precipitate. Separate the crystals on a funnel with suction (sintered glass disc), press out excess liquid, transfer into another test tube, and add 4-5 ml of water. Shake the mixture: the crystals completely dissolve. Add 1 ml of dilute hydrochloric acid: benzoic acid precipitates.

B. Transfer the filtrate (obtained after separation of potassium benzoate crystals) into a test tube and heat on a water bath to evaporate the greater part of alcohol.

The residue on evaporation has the odour of benzyl alcohol Place a part of the residue into a test tube, add 1-2 ml of water, a small amount of potassium dichromate, and 1 ml of concentrated sulphuric acid. Heat the mixture and note the specific odour of the original aldehyde. Carefully add, drop by drop, 2 ml of concentrated sulphuric acid to the remaining quantity of benzyl alcohol and heat the mix-

ture: benzyl alcohol is specifically resinified (characteristic of benzyl alcohol).

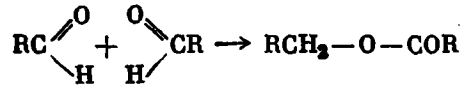
Benzaldehyde reacts with alkali to give benzyl alcohol and a benzoate:



One molecule of the aldehyde is oxidized and the other reduced.

It has recently been established that in the course of the reaction, hydride ion, i.e. the hydrogen atom with its own electron pair, passes from the carbonyl group of one aldehyde molecule to the carbonyl carbon of the other molecule. Solvent does not take part in this 'hydride transfer'.

It was first understood that only aromatic aldehydes were capable of such conversions (Cannizzaro reaction), but V. E. Tishchenko showed in 1900-1905 that this reaction is general and can be realized with fatty compounds as well (cf. Experiment 63). The first step of the reaction is formation of ester:



which is then saponified by alkali. If aluminium alcoholate is used instead of alkali, ester is also formed, but it is not saponified.

V. M. Rodionov developed a method for carrying out this reaction in water-alkali solution with a mixture of aromatic aldehyde and formaldehyde. The latter is acidified to formic acid to reduce aromatic aldehyde to the corresponding alcohol.

Mutual oxidation and reduction of aldehydes is an important reaction in many biological processes, for instance, in various fermentation processes.

Unlike benzaldehyde and benzoic acid, benzyl alcohol (b.p. 206 °C) is easily resinified by concentrated sulphuric acid. Benzyl alcohol reacts with other substances (organic acids, hydrohalic acids, sodium metal, oxidants) like fatty alcohols (cf. Chapter 6).

181
Oxidation of Benzaldehyde

REAGENTS

Benzaldehyde.
Silver oxide, ammoniacal solution (see Experiment 60).
Ethyl alcohol.

A. Place a drop of benzaldehyde on a glass plate and keep in air for a few hours. Crystals of benzoic acid appear on the glass. They

are readily soluble in alkali solutions and hot water; sparingly soluble in cold water.

B. Thoroughly wash a test tube (see Experiment 60) and place into it 1 ml of ammoniacal silver oxide solution and a drop or two of benzaldehyde. Heat the mixture on a water bath and note the changes, if any.

C. Add 2-3 ml of potassium permanganate solution to 1-2 drops of benzaldehyde and heat the mixture on a water bath with shaking until the odour of aldehyde is felt no longer. Destroy the violet colouration (excess permanganate) by adding a few drops of alcohol and pass the mixture through a small pleated filter. Precipitate benzoic acid from the colourless filtrate by acidifying with dilute sulphuric acid.

Benzaldehyde can easily be acidified to benzoic acid not only with oxidants, but with atmospheric oxygen as well. Perbenzoic acid, C_6H_5COOOH, is first formed. It has the structure of the peroxide (cf. explanations to Experiment 260).

Oxidation of benzaldehyde with atmospheric oxygen is the homolytic reaction having the radical-chain mechanism. Oxidation with permanganate is a heterolytic reaction. Its mechanism is very complicate: it begins with attachment of the hydrogen ion, proton, which catalyses the reaction, to the carbonyl oxygen. The second oxygen atom is accepted by benzoic acid only from the permanganate molecule (see also explanations to Experiment 19).

Benzaldehyde gives the reaction with Schiff's reagent, but unlike fatty aldehydes, it does not reduce Fehling's solution. In the reaction with benzaldehyde, bromine is not attached to the benzene ring, but substituted for the hydrogen of the aldehyde group to form benzoyl bromide, C_6H_5COBr.

182
Preparing Benzoic Acid by Oxidation of Toluene

REAGENTS

Toluene.
Potassium permanganate, powder.
Sodium sulphite.

Carry out the reaction in a 100-200 ml round-bottomed flask. Mount a 'cold-finger' condenser in the flask neck using a split plug with a hole (see Fig. 3*b*,*c*).

Place in the flask 1.5 g of potassium permanganate, 25 ml of water, 0.5 ml of concentrated alkali solution, 1 ml of toluene and a boiling stone. Install the condenser, heat the mixture on a gauze over a bur-

ner, and boil for 60-90 minutes. The reaction can be considered complete when the colour of the permanganate vanishes or toluene drops are no longer observed in the aqueous condensate on the flask walls and the condenser.

Cool the mixture, acidify with dilute sulphuric acid until congo test paper turns intense blue (cf. Experiment 75), and add solid sodium sulphite in small portions (or its concentrated solution) until the colour vanishes and the precipitate dissolves. Transfer the liquid into a beaker or a dish and heat on a gauze over a burner to reduce the volume of the solution by about 50 per cent. Cool the residue and in 30-60 minutes, separate the crystals on a filter with suction. Press out excess liquid. The yield of benzoic acid is about 0.5 g. To purify the acid, re-crystallize it from water (see Experiment 1).

183
Preparing *o*-Phthalic Acid by Oxidation of Naphthalene

REAGENTS

Naphthalene.
Potassium permanganate, powder.
Sodium sulphite.

Oxidize naphthalene using the same procedure as described in Experiment 182 (oxidation of toluene), but it is more convenient to use a water-cooled reflux condenser instead of the 'cold-finger' condenser, since much naphthalene accumulates in the condenser tube at the beginning of the process, and it becomes necessary to push the crystals back into the flask with a long glass rod.

Place 1 g of naphthalene into a reaction flask, add 5 g of potassium permanganate, 70 ml of water, and 0.5 ml of concentrated alkali solution. Oxidize for about two hours. The further procedure is the same as in the previous experiment.

Purify phthalic acid by re-crystallization from hot water.

The acid can be used in Experiments 190 and 230 without purification.

Benzene is quite stable to oxidants (see Experiment 154). Benzene homologues are oxidized comparatively easily to give aromatic acids, each lateral chain of the benzene nucleus, irrespective of its lenght, turning into a carboxylic group. The number and the arrangement of these groups in the product of oxidation is indicative of the structure of the oxidized substance.

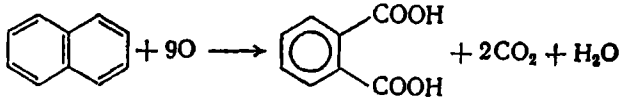
In Experiment 182, the reaction is as follows:

$$C_6H_5CH_3 + 2KMnO_4 \longrightarrow C_6H_5COOK + 2MnO_2 + KOH + H_2O$$

Other substances can be oxidized in these conditions as well. For example, *o*-nitrotoluene (see Experiment 160) can be oxidized to *o*-nitrobenzoic acid (m.p. 147 °C), and *m*-xylene to isophthalic acid (m.p. 348 °C). Doubled quantities of water and permanganate should be used for oxidation of xylene.

When melted, phthalic acid partly converts into anhydride, and its melting point is not therefore sharp.

Naphtalene is oxidized according to the equation:



It follows that one of the condensed benzene rings of naphthalene is oxidized like two lateral chains in the ortho position. This method (conversion into substituted phthalic acids) is often used to determine the structure of naphthalene derivatives.

As a rule, alkaline solutions boil with bumps, and a boiling stone should therefore be added (Experiments 182 and 183). If for some reason boiling is suspended, add a new piece of stone before resuming boiling.

Do not separate by filtration or discard manganese dioxide precipitate, since it contains considerable part of carboxylic acid and its salt that fail to be removed even by washing with hot water. It is not essential in qualitative Experiment 154 though.

184
Comparison of Ionization Degree of Benzoic and Salicylic Acids

REAGENTS

Benzoic acid.
Salicylic acid.
Sodium bicarbonate.
Sodium acetate.
Sodium formate.

Triturate the acids into a fine powder.

Prepare solutions of bicarbonate, acetate, and formate of sodium in test tubes, by shaking 1-g portions of the salts with 5 ml of water for a few minutes. Sodium bicarbonate is only sparingly soluble and part of it remains in precipitate. The other two salts dissolve completely.

Divide each solution into two parts. Add a small quantity of benzoic acid to one part and approximately the same quantity of sali-

cylic acid to the other part of the solution. Shake the mixtures and note in which salt solution the acid dissolves. Make sure that the same quantity of the acid does not dissolve in an equal volume of pure water.

As a rule, carboxylic acids of the aromatic series are sparingly soluble in water. Ionization degrees of the acids differ greatly. Substituted acids, having nitro groups, halogen atoms, or hydroxyl groups in the benzene ring, are usually stronger ionized. This is especially so if the halogen atom or the hydroxyl group is in the ortho position to the carboxyl.

For example, salicylic acid ($K = 1 \times 10^{-3}$) is much stronger than meta- and para-hydroxybenzoic acids. The presence of the hydrogen bond between the hydroxyl hydrogen and the carbonyl oxygen of the carboxyl group increases the positive charge on the carboxyl carbon to sharply increase the ionization of the acid.

Sodium salts of even sparingly soluble acids are as a rule readily soluble in water.

The method can be used for approximate assessment of the ionization degree (strength) of acids sparingly soluble in water by trying whether or not it displaces another acid (from its salt) whose ionization degree is known (cf. Experiments 75 and 76). If the acid in question dissolves in a salt of another acid, it means that the former displaces the weaker acid from its salt. For example, dissolution of benzoic acid in sodium acetate solution indicates that benzoic acid ($K = 6.6 \times 10^{-5}$) displaces a weaker acetic acid:

$$C_6H_5COOH + CH_3COONa \longrightarrow C_6H_5COONa + CH_3COOH$$

Formic acid is stronger than benzoic but weaker than salicylic acid, and the latter therefore dissolves in solutions of all the three salts, whereas benzoic acid dissolves only in sodium bicarbonate and sodium acetate solutions.

Almost all carboxylic and sulphonic acids are soluble in sodium bicarbonate solution. Phenols and enols are as a rule insufficiently dissociated and do not dissolve in it (except substances readily soluble in water). Dinitrophenol, trinitrophenol, and tribromophenol are soluble in $NaHCO_3$ like true acids (cf. Chapter 13).

Sodium benzoate is often used for home canning of berries, fruits, and juices. The salt is taken in the quantity of 0.1-0.15 per cent of the mass of the material. The preservative is harmless.

185
Reaction of Benzoic and Salicylic Acids with Ferric Chloride

REAGENTS

Benzoic acid.
Salicylic acid.
Ethyl alcohol.

Prepare saturated solutions of benzoic and salicylic acids by shaking their small quantities with 7-8 ml of water. Decant the clear liquids and use them in this and further experiments (Experiments 186 and 187).

Add a few drops of ferric chloride solution to 1-2 ml of each acid. One solution turns deep violet. Add an equal volume of alcohol to this solution and see if the colour vanishes (cf. Experiment 168).

The colour reaction with ferric chloride is characteristic of many compounds having the phenol hydroxyl group in the molecule. Out of the three isomers of hydroxybenzoic acids, the meta isomer does not give this reaction. *o*-Hydroxybenzoic (salicylic) and *p*-hydroxybenzoic acids give the colour reaction with ferric chloride, the colour vanishing on addition of strong mineral acids or alkalis. But alcohol, glycerol, and acetic acid fail to remove the colour (unlike with iron phenolate, cf. Experiment 168). Benzoic acid does not form coloured complex compounds with iron salts.

186
Reaction of Benzoic and Salicylic Acids with Bromine

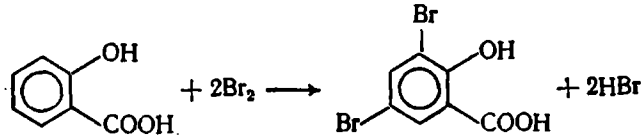
REAGENTS

Benzoic and *salicylic acids*, saturated solutions (see Experiment 185)
Potassium iodide, 1 per cent solution.
Benzene.

A. Place 1-2 ml of each acid into separate test tubes, add bromine water drop by drop, and note the changes, if any.

B. Continue adding bromine water into the test tube containing salicylic acid with shaking until a persistent bright yellow colour develops and the white precipitate turns yellowish. Boil the obtained mixture for 2-3 minutes to remove excess bromine. The precipitate dissolves. Cool the test tube, add 0.5 ml of benzene, and shake: the yellow precipitate that fell out on cooling dissolves again. Add a few drops of potassium iodide and shake: the liberated iodine colours the benzene layer red-violet.

The carboxyl group only slightly affects the mobility of the hydrogen atoms at the benzene-ring carbons, but the introduction of the phenol hydroxyl sharply increases their mobility (see explanations to Experiment 116). Benzoic acid is not therefore brominated in the conditions of the experiment, while salicylic acid is brominated very quickly to form first the colourless and sparingly soluble 3,5-dibromosalicylic acid (m.p. 228 °C)



Excess bromine eliminates the carboxyl group in the form of CO_2 and replaces it to form tribromophenol. The latter then turns into a yellow tetrabromide by further bromination (see Experiment 167). The tetrabromide is an oxidant and it liberates iodine from potassium iodide solution.

187
Comparison of Oxidabilities of Benzoic and Salicylic Acids

REAGENTS

Benzoic and *salicylic acids*, saturated solutions (see Experiment 185).

Place 1-2 ml of each acid in separate test tubes and add equal volumes of sodium carbonate solution. Then add dropwise potassium permanganate solution with shaking until the colour stabilizes. Note the different course of the reactions in the test tubes.

Like the previous experiments (Experiments 185 and 186), the given reaction illustrates the different properties of benzoic and salicylic acids. The difference is caused by the presence of the phenol hydroxyl in the molecule of salicylic acid. Like phenols, salicylic acid is readily oxidized in an alkaline medium with potassium permanganate to give a complicate mixture of the reaction products.

188
Nitration of Salicylic Acid

REAGENTS

Salicylic acid.

Use the HOOD.

Place about 0.05-1 g of salicylic acid into a test tube and add 1 ml of concentrated nitric acid. Shake the mixture and heat slightly:

an energetic reaction, with liberation of heat and nitrogen oxides, begins. The crystals of salicylic acid dissolve, and yellow powder of nitrosalicylic acid precipitates.

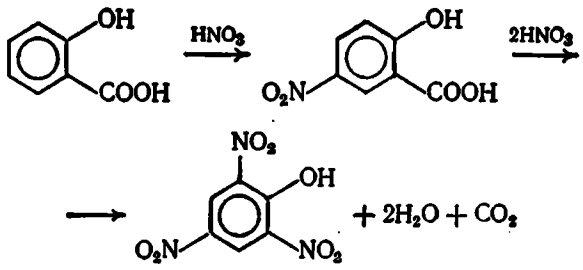
A. Shake the mixture in 5-6 minutes, transfer several drops into another test tube, and dilute with 6-10 volumes of water. Divide the yellow solution into two parts. Add excess dilute alkali solution to one portion until it turns orange. To the other portion, add as much of the alkali solution as will not change the colour of the mixture, and then 2-3 drops of ferric chloride solution: the mixture turns bright red (cf. Experiment 185).

B. Add 1 ml of concentrated nitric acid to the mixture of nitrosalicylic and nitric acids (Test A) and boil for a few minutes over a burner. The precipitate of nitrosalicylic acid soon dissolves. Pour the obtained clear solution into five volumes of cold water, heat again until the mixture becomes clear (if there was a precipitate), and allow to cool slowly. Needles of trinitrophenol crystals precipitate in a few minutes.

The presence of residual quantities of nitrosalicylic acid in the obtained solution can be detected by ferric chloride.

Salicylic acid, having the phenol character, is easy to nitrate. 5-Nitrosalicylic acid (m.p. 227 °C) is first predominantly formed. Like many nitrophenols, its acid solution is yellow, and alkaline orange (cf. Experiments 172 and 173). When ferric chloride is added, all isomers of nitrosalicylic acid turn specifically red.

Further nitration is much slower, and nitrosalicylic acid is gradually converted into trinitrophenol with elimination of the carboxyl group in the form of CO_2:



Unlike nitrosalicylic acid, trinitrophenol does not give colour reaction with ferric chloride.

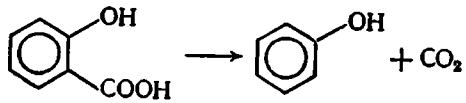
189
Action of Heat on Benzoic and Salicylic Acids

REAGENTS

Salicylic acid.
Benzoic acid.

Place small quantities of each acid into separate dry test tubes and melt them over a burner until they begin boiling. Continue the heating seeing to it that not only the bottom of the test tube but also its walls are heated so that the vapour of the boiling acid passes through a hot zone. The acids are partly sublimed, and specific odour is felt from one test tube. The odour persists on cooling.

The easiness with which aromatic acids decompose on heating depends on the presence and position of substitutes in the benzene ring. Benzoic acid stands heating up to 400 °C, while salicylic acid is carboxylated to phenol at 230-250 °C:



p-Hydroxybenzoic acid is more stable: carbon dioxide is eliminated only at 300 °C. *m*-Hydroxybenzoic acid is almost as stable as benzoic acid and distils without decomposition.

190
Formation of Phthalic Anhydride

REAGENTS

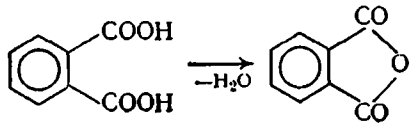
Phthalic acid (see Experiment 183).
Benzene.

A. Place about 0.1-0.2 g of dry phthalic acid in a dry test tube and heat over a burner holding the test tube horizontally. The acid melts and sublimes to form a white deposit on the colder parts of the test tube.

Allow the test tube to cool and then heat the white sublimate holding the test tube in the inclined position. Unlike the original acid, phthalic anhydride easily melts and drips downwards.

B. Add 1-2 ml of benzene to the same test tube. Place a small quantity of phthalic acid into another test tube and add an equal volume of benzene. Note the different solubility of the acid and its anhydride in benzene.

Phthalic acid readily eliminates water (even at temperatures below 180 °C) to give phthalic anhydride:



Phthalic anhydride (m.p. 131 °C) is widely used in industry for synthesis of anthraquinone and phthalein dyes (Experiment 230), resins, and many other products. Unlike phthalic acid, it does not contain free hydroxyl groups and is therefore better soluble in non-polar solvents, for instance, in benzene.

191
Formation and Saponification of Aromatic Acid Esters

REAGENTS

Benzoic acid.
Salicylic acid.
Ethyl alcohol, rectified.

A. Place 5 ml of alcohol in a test tube, and carefully add, with shaking, 2 ml of concentrated sulphuric acid. Divide the hot liquid into two equal portions and add 0.5 g of benzoic acid to one and 0.5 g of salicylic acid to the other portion. Heat both mixtures on a boiling water bath for 10-15 minutes, then transfer the test tubes into a beaker containing cold water, and add 10 ml of water into each mixture.

The formed ester, whose odour can be felt even at the beginning of the experiment, rises to the surface, above the aqueous layer. Ethyl salicylate can also be formed at the bottom of the test tube in a mixture with the crystals of unreacted salicylic acid.

B. Pipette a few drops of the obtained ethyl benzoate into a clean test tube, add 1 ml of concentrated alkali solution, and heat the mixture on a boiling water bath for 5-10 minutes with shaking at short intervals. The time is insufficient for completion of the saponification of the ester (cf. Experiment 93) but when the mixture is cooled and acidified with hydrochloric acid, crystals of benzoic acid precipitate from the aqueous solution.

192
Preparing Ethyl Benzoate

REAGENTS

Benzoic acid.
Ethyl alcohol, crude or rectified.
Sodium chloride, saturated solution.

Place 6 ml of alcohol in a flask or a large test tube, add 5 ml of concentrated sulphuric acid with adequate cooling, then add 5 g of benzoic acid, and wash off its crystals from the test tube walls with another 5 ml of alcohol. Connect a reflux condenser, or a straight tube condenser, and heat the mixture on a boiling water bath for 90-120 minutes.

Cool the mixture and transfer it into 50 ml of saturated sodium chloride solution. Separate the oil, wash it with 5 ml of soda solution, then again with sodium chloride, separate from the liquid, dry with a piece of potash, and distil from a test tube with a side arm soldered close to the bottom. The ester is almost completely distilled at 206-208 °C. The yield is 2.5-3.5 g. The product can be used in Experiment 257.

193
Preparing Dimethyl Phthalate

REAGENTS

Phthalic anhydride.
Methyl alcohol.

Place 5 ml of methyl alcohol and 2 g of phthalic anhydride into a test tube and then carefully add with shaking 2 ml of concentrated sulphuric acid. See to it that the mixture does not boil. Place the test tube on a boiling water bath and shake with stirring by a glass rod for 10-15 minutes until phthalic anhydride is all dissolved. Heat the mixture for another 2-3 minutes, then allow the test tube to cool slightly and transfer its contents into a beaker or a flask containing 50-60 ml of cold water.

The product is a heavy oil. Decant the supernatant water, add a new portion of water, shake, and then wash with sodium bicarbonate solution. Transfer the washed oil by a pipette into a dry test tube and dry with a piece of calcium chloride with slightly heating until the oil is clear. The yield is about 2 g. The product can be distilled from a test tube with a thermometer and a low side arm (see Fig. 8). Test the obtained ester for easiness of saponification with alkali (see Experiment 191, B).

The formation and hydrolysis of carboxylic ester were discussed earlier (Experiments 93-95). The rate of esterification of aromatic acids differs and depends on the acid structure, e.g. on the number and position of substitutes in the benzene ring. The presence of substitutes in the ortho position with respect to the carboxyl group usually retards the esterification process (steric hindrances). It is therefore more difficult to esterify salicylic than benzoic acid.

Dibasic phthalic acid can react with alcohols to give both acid and neutral esters. The latter are predominantly formed with excess alcohol. Phthalic anhydride reacts with alcohols faster than phthalic acid (cf. Experiment 97). Volatility of esters usually decreases with the growing hydrocarbon radical of alcohol, whereas the viscosity increases. Dialkyl phthalates (e.g. dibutyl, diisobutyl, and other similar phthalates) are widely used as plasticizers in many synthetic polymers, for instance, various lacquers, PVC, etc., that are otherwise very brittle. Dimethyl phthalate's volatility is the highest of other phthalic esters. It is used as insect repellent. Flies, mosquitoes, and other biting and blood-sucking insects usually do not land on the skin oiled with dimethyl phthalate.

Esters of aromatic acids are as a rule characterized by specific odour. They are sparingly soluble in water and slowly undergo hydrolysis even in alkaline medium. Precipitation of benzoic acid in Experiment 191, B indicates that the ester can still undergo partial hydrolysis.

194
Formation of Benzoyl Chloride

REAGENTS

Benzoic acid.
Phosphorus pentachloride.

Use the HOOD.

Place 0.5 g of benzoic acid in a wide test tube and carefully add, with shaking, 0.5-1 g of ground phosphorus pentachloride. The mixture becomes hot and gradually thins. Shake the test tube for a few minutes until the mixture is thin and solid particles disappear. Slight heating is sometimes required.

Cool the liquid and carefully add, drop by drop, its small portion to 2-3 ml of cold water containing ice or snow. While doing it, shake the test tube energetically. A heavy oil is formed. Note its specific odour. Carefully transfer the remaining (greater) part of the reaction mixture into another test tube containing 5 ml of concentrated ammonia solution and 5 ml of water. Cool the test tube in a beaker with water. Benzamide crystals precipitate from the cold water-ammonia solution (see Experiment 197).

Phosphorus pentachloride reacts with carboxylic acids to substitute chlorine atom for the hydroxyl of the carboxyl group. The general equation of the reaction is as follows:

$$RCOOH + PCl_5 \longrightarrow RCOCl + HCl + POCl_3$$

Gaseous hydrogen chloride leaves the reaction sphere, and the remaining mixture of phosphorus oxychloride (*b.p.* 107 °C) and the chloride of the starting acid can be separated by distillation.

In cold water $POCl_3$ is hydrolysed faster than benzoyl chloride, and the latter can be identified by the odour and appearance.

If excess ammonia solution is added to the reaction mixture, several products are formed. Chlorine atoms of all compounds contained in the mixture are united in ammonium chloride. At the same time, phosphorus oxychloride and the starting phosphorus pentachloride give ammonium phosphates; benzoic acid gives the ammonium salt, and benzoyl chloride gives benzamide, $C_6H_5CONH_2$ (Experiment 197). Of all these substances, only benzamide is sparingly soluble in cold water and its formation proves the conversion of benzoic acid into benzoyl chloride.

195
Reactions of Benzoyl Chloride

REAGENTS

Benzoyl chloride.
Hydroxylamine hydrochloride, 5 per cent solution.

A. Place 1 ml of water in a test tube and add 3-4 drops of benzoyl chloride. It lowers to the bottom and does not dissolve on shaking. Heat the mixture to low boil for a few minutes to dissolve benzoyl chloride and until its pungent odour disappears. Now cool the test tube in a beaker with water. Crystals of benzoic acid gradually precipitate from the solution. Add a few drops of alkali solution: the crystals dissolve.

B. Place 1 ml of hydroxylamine hydrochloride into a test tube and add a drop of benzoyl chloride. Heat the mixture to boiling, then cool, and add 1-2 drops of ferric chloride solution. The liquid becomes brightly coloured.

The reactions of benzoyl chloride are less energetic than those of acetyl chloride (see Experiment 96 and explanations to it), because the decreased electron density at the oxygen- and chlorine-bonded carbon is partly compensated by the shift of π-electrons of the benzene ring in its direction. Like chlorides of higher fatty acids, benzoyl chloride is slowly hydrolysed by water (see also Experiment 196).

Benzoyl chloride easily reacts with hydroxylamine to give benzohydroxamic acid, $C_6H_5CONHOH$, whose complex salt with iron

is deep violet in solution (cf. Experiments 111 and 113). Unlike acetamide, benzamide does not produce hydroxamic acid in these conditions.

In order to destroy residual amounts of benzoyl chloride, whose vapour causes tears, rinse the glassware with dilute ammonia solution and then wash with water.

196
Benzoylation of Alcohols and Phenols

REAGENTS

Benzoyl chloride.
Ethyl alcohol, rectified.
Glycerol.
Phenol.

A. Mix, in a test tube, 1 ml of benzoyl chloride with 2 ml of alcohol. A homogeneous solution is formed. The reaction is not exothermic. Add this solution, in small portions (within 1-2 minutes), to 3 ml of dilute alkali solution with shaking energetically. The mixture becomes hot, the odour of benzoyl chloride gradually vanishes, and an aromatic layer of ethyl benzoate rises to the surface of the mixture.

B. Take two test tubes prodived with tightly fitting stoppers. Place 1 ml of glycerol into one, and 1 g of phenol into the other test tube. Add 3 ml of water and 2 ml of concentrated alkali solution into both test tubes and shake to obtain a homogeneous solution. Now add, in small portions, 1 ml of benzoyl chloride. Each portion should contain a few drops of the reagent. After adding each new portion, close the test tube with a stopper and shake energetically. From time to time cool the test tube in a beaker with cold water. In both tubes the reactions are exothermic, and the reaction products crystallize out of oily drops.

Both products thus obtained can be re-crystallized from water and alcohol mixture. Pure substances can also be isolated in the form of oil. To initiate crystallization, leave a few crystals of the product, and during re-crystallization, drop them into the cooled solution.

Alcohols and phenols react with acid chlorides to give esters:

$$ROH + ClCOR' \longrightarrow ROCOR' + HCl$$

The liberated hydrogen chloride is bound with alkali, and the reaction is accelerated.

Benzoic esters are sparingly soluble in water and slowly hydrolysed in the conditions of this experiment. Many esters well crystallize

and have specific melting points. For example, glycerol tribenzoate, $CH_2(OCOC_6H_5)CH(OCOC_6H_5)CH_2(OCOC_6H_5)$, melts at 76 °C, and phenyl benzoate, $C_6H_5OCOC_6H_5$, at 68 °C. Benzoylation with benzoyl chloride in an alkaline medium is often used for isolation and identification of alcohols and phenols, since the benzoylation rate of these substances is much higher than the rate of hydrolysis of acid chloride itself (see Experiment 195). This method can be used to isolate alcohol or phenol (as the corresponding benzoic ester) from their very dilute aqueous solutions. The process is known as the Schotten-Baumann reaction.

197
Preparing Benzamide and Its Hydrolysis

REAGENTS

Benzoyl chloride.

A. Place 2 ml of concentrated aqueous ammonia in a test tube and carefully add, drop by drop, 1 ml of benzoyl chloride, with cooling and shaking. The mixture becomes hot, the drops of benzoyl chloride quickly dissolve, its odour disappears, and a white precipitate forms. If the odour of benzoyl chloride can still be felt on completion of the reaction, add a few drops of ammonia solution.

Add, with shaking, 2-3 ml of cold water to the reaction mixture, allow it to stand for a few minutes, and decant the liquid. Wash the precipitate several times by shaking with small portions (2-3 ml) of cold water and carefully decant the liquid. Now add 2-3 ml of water to the washed product and heat the mixture on a water bath with shaking to dissolve the precipitate.

Slowly cool the liquid: benzamide crystals precipitate. The yield is 0.8-0.9 g.

B. Mix a small portion of benzamide crystals with 3-4 ml of alkali solution and heat to boiling: the crystals dissolve, and ammonia is liberated. Cool the obtained liquid and see whether or not benzamide crystals precipitate. Acidify the liquid with hydrochloric acid: the crystals precipitate.

Ammonia reacts with acid chloride to give the corresponding amide:

$$RCOCl + NH_3 \longrightarrow RCO{-}NH_2 + HCl$$

The liberated hydrogen chloride is bound with excess ammonia into ammonium chloride that can be removed by washing with water.

Aromatic acid amides are usually sparingly soluble in cold water (cf. Experiment 195). When heated with acids or alkalis they are hydrolysed according to the equation:

$$RCO-NH_2+H_2O \longrightarrow RCO-OH+NH_3$$

The formation of ammonia in an alkaline medium is revealed at once; another reaction product, organic acid, can be isolated either free (if it is sparingly soluble, like benzoic acid) or in the form of a sparingly soluble salt.

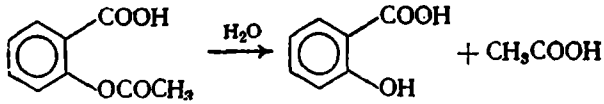
198
Hydrolysis of Acetylsalicylic Acid

REAGENTS

Acetylsalicylic acid.

Dissolve a few crystals of acetylsalicylic acid in 3-5 ml of water. Divide the solution into two parts. Boil one portion for 2-3 minutes, then cool, and add a few drops of ferric chloride solution into each test tube.

Acetylsalicylic acid does not produce a colour reaction with ferric chloride, since the phenol hydroxyl in its molecule is acetylated. Hydrolysis of acetylsalicylic acid, which is an ester of acetic acid, not of salicylic acid (cf. Experiment 191), is effected very easily even in the absence of acids or alkalis:



The formation of free salicylic acid can be detected by the specific reaction with ferric chloride (see Experiment 185).

199
Reactions of Cinnamic Acid

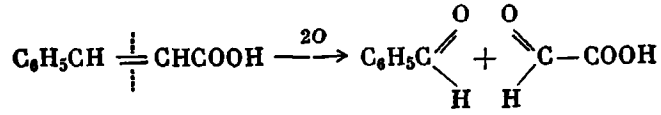
REAGENTS

Cinnamic acid.

A. Place a few crystals of cinnamic acid in a test tube, add 1 ml of water and 8-10 drops of potassium permanganate, and shake the mixture. The colour changes at room temperature. Slightly heat the mixture and note the rapid change in its appearance. Specific fragrant odour can be felt.

B. Repeat the procedure using bromine water instead of potassium permanganate. The reaction mixture does not require heating.

Like other unsaturated compounds derived from ethylene (see Experiment 19), cinnamic acid is oxidized at the double bond. The oxidation of cinnamic acid gives glyoxylic acid and benzaldehyde. The presense of the latter is easy to detect by its specific odour:



In the presence of excess potassium permanganate both products can further oxidize.

Attachment of bromine at the double bond of cinnamic acid molecule gives β-phenyl-α,β-dibromopropionic acid, $C_6H_5CHBrCHBrCOOH$ (cf. Experiment 18).

200
Reactions of Gallic and Tannic Acids

REAGENTS

Gallic acid.
Tannic acid.
Ferrous sulphate, 3 per cent solution, prepared for the experiment.

Carry out simultaneously tests with gallic and tannic acids. Dissolve 0.2-0.3 g of the acid in 3-5 ml of water and divide the obtained solutions into three parts.

A. Add 5-6 drops of dilute alkali solution to the first part, and allow to stand for 10-15 minutes: the colour of the solutions changes beginning with the upper layers.

B. Add 2-3 drops of ferric chloride solution to the second part of the starting solution.

C. Add 0.5 ml of ferrous sulphate to the remaining portion. Using a splint or a glass rod, make an inscription with the obtained slightly coloured solution on a sheet of paper. Keep the paper in the air for a few days: the inscription gradually darkens and becomes quite distinct.

Gallic acid is a polyhydric phenol and possesses many of the properties of phenols (see Experiments 168-170). It is easily oxidized, especially in an alkaline solution even with atmospheric oxygen to form dark coloured products. The reaction with ferric chloride is also characteristic of phenols. Gallic acid does not give a colour reaction with ferrous salts, but as iron is oxidized gradually with

atmospheric oxygen into its tervalent state, the mixture containing gallic acid blackens.

Tannins, isolated from some plants, are mixtures of esters of glucose and acids, mainly gallic and *m*-galloylgallic. Like free gallic acid, tannins are readily oxidized and give an intense colour reaction with ferrous salts.

201
Colour Reactions of Lignin

REAGENTS

Aniline (solution of 5 ml of aniline and 6 ml of concentrated hydrochloric acid in 200 ml of water).

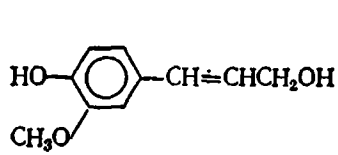
Phloroglucinol, 0.05-0.1 per cent solution in dilute hydrochloric acid.

Carry out simultaneously tests with a smooth wooden board, a piece of common cheap paper, and a piece of filter paper.

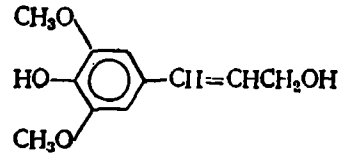
Using a glass rod, place a drop or two of aniline solution and phloroglucinol solution onto each material. The solution of aniline salt produces a bright yellow spot on wood and paper. The phloroglucinol solution spot is first colourless and then rapidly turns red. The solutions do not colour filter paper.

The natural polymer lignin is a constituent of wood (to 20-30 per cent of its dry weight).

Presumably, lignin of coniferous plants is a polymer of the products of oxidation of coniferyl alcohol, whereas lignin of leaf-bearing trees contains syringenin as well:



coniferyl alcohol



syringenin (sinapyl alcohol)

Part of phenol hydroxyls of lignin is bound in plant tissues with monosaccharide residues.

Compared with cellulose, lignin is stabler to hydrolysis, but easier decomposed by oxidation. Lignin gives characteristic colour reactions with many phenols and amines in an acid medium.

Cheap paper contains lignin since disintegrated wood is its constituent part.

AROMATIC AMINES AND NITROSO COMPOUNDS

Table 13 gives compounds that will be used in experiments included in this chapter. Dimethylaniline and diphenylamine should be kept in the laboratory ready for use, whereas the other substances can be prepared in the course of the experiment.

202
Preparing Aniline

REAGENTS

Nitrobenzene.
Iron, filings.
Tin, granules.

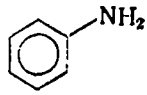
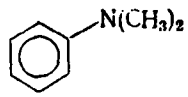
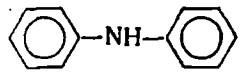
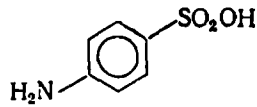
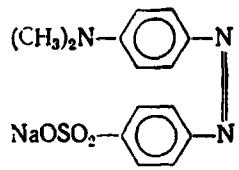
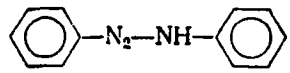
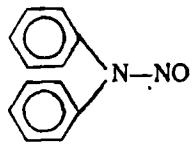
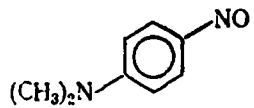
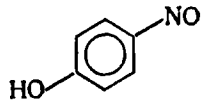
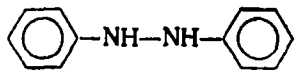
A. Place 10 g of iron filings, 4 ml of water, and about 0.3 ml of concentrated hydrochloric acid in a small round-bottomed flask. Close the flask with a plug through which a bent outlet tube is passed (Fig. 14), and turn the orifice of the tube upwards. Heat the mixture over a burner and boil for 1-2 minutes: hydrogen is liberated. Add 1 ml of nitrobenzene, stopper the flask again, and shake the mixture, first carefully and then strongly. Heat the mixture again and maintain it boiling for 1-2 minutes, then place the flask on a boiling water bath and keep there for 10-15 minutes with strongly shaking at short intervals.

After adding nitrobenzene, evolution of hydrogen almost stops; part of iron turns into red-brown oxide of di- and tervalent iron.

When the odour of nitrobenzene disappears, remove the flask from the bath, wipe it on the outside, and add 8-10 drops of dilute alkali solution to the hot reaction mixture with shaking until the solution reacts strongly alkaline. Now add 2 ml of water and fix the flask in the inclined position in the stand. Connect the outlet tube again and lower its end into a receptacle cooled with water.

Table 13

Boiling and Melting Points of Aromatic Amines and Nitroso Compounds

Substance	Formula	M. p., °C	B. p., °C
Aniline, density 1.03 g/cc		−6	184
Dimethylaniline, density 0.96 g/cc		2	193
Diphenylamine		54	302
Sulphanilic acid		288 (decomp.)	—
Sodium para(para-dimethylamino-phenylazo)-benzene sulphonate (methyl orange)		Decomposes	—
Diazoaminobenzene		98	Decomposes
N-Nitrosodiphenylamine		66	—
p-Nitrosodimethylaniline		92	—
p-Nitrosophenol		120	—
Hydrazobenzene		126	—

Start distillation by heating carefully first the upper layers of the reaction mixture over a burner. About 2 or 3 ml of aniline-water mixture are quickly distilled into the receptacle. The mixture is cloudy. Stop distillation and dismantle the apparatus.

A yellowish oily layer of aniline separates from the distillate on standing.

B. Place 2 ml of nitrobenzene, 9 ml of concentrated hydrochloric acid, and 5 g of tin into a flask provided with an outlet tube (see A). The mixture becomes hot. Heat it to a low boil with shaking at short intervals for 20-25 minutes until the nitrobenzene odour disappears. See to it that the outlet tube is directed upwards. Cool the mixture, add 10 ml of water and concentrated alkali solution until the mixture reacts strongly alkaline, and until almost all tin compounds are dissolved, add a boiling stone, and distil the aniline-water mixture (see above).

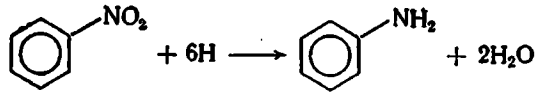
Keep the obtained aniline for Experiments 203-205 and 209.

To purify aniline, separate it by a pipette, dry with a piece of solid alkali, and distil. The yield of product is about 50 per cent of the weight of the starting nitrobenzene.

Do not inhale aniline vapour (see Chapter 2).

Aniline was prepared in 1840 by the Russian academician Fritzsche by heating indigo with alkali. N. N. Zinin, in 1841 in Kazan, discovered the method of converting aromatic nitro compounds into amines (reduction of nitrobenzene to aniline). This discovery lay the basis for the manufacture of synthetic dyes.

Nitrobenzene is reduced through a series of intermediate reactions, and aniline is the final product. The process can be shown schematically as follows:



First Zinin used ammonium sulphide as the reducing agent, but it was found that nascent hydrogen liberated by the action of metal on acid is a better reductant:

$$Fe + 2HCl \longrightarrow FeCl_2 + 2H$$

Hydrochloric acid is constantly regenerated since basic ferric chloride that is formed by oxidation of ferrous chloride with nitrobenzene is again reduced by excess metallic iron:

$$2FeCl_2 + O + H_2O \longrightarrow 2FeCl_2(OH)$$

$$6FeCl_2(OH) + Fe + 2H_2O \longrightarrow 2Fe_3O_4 + FeCl_2 + 10HCl$$

The source of hydrogen is thus water, and the summary reaction of nitrobenzene reduction can be expressed as follows:

$$4C_6H_5NO_2 + 9Fe + 4H_2O = 3Fe_3O_4 + 4C_6H_5NH_2$$

In order to activate iron filings, they should be boiled with acid before adding nitrobenzene. The thin film of oxides on the iron surface is thus dissolved. Ferrous chloride is a catalyst in this process and it can be replaced by chlorides of other metals if sulphuric acid is used in the process instead of hydrochloric acid.

The reaction with tin occurs according to the following summary equation:

$$2C_6H_5NO_2 + 3Sn + 12HCl \longrightarrow 2C_6H_5NH_2 + 3SnCl_4 + 4H_2O$$

Aniline reacts with hydrochloric acid that is present in the reaction mixture (see Experiment 203) to give salt. To recover aniline, alkali should therefore be added. When tin is used in the process, the quantity of alkali should be increased since it is needed not only for decomposition of the double salt of aniline hydrochloride and stannic chloride, $SnCl_4 \cdot 2C_6H_5NH_2 \cdot 2HCl$, but also for conversion of stannic hydroxide into a soluble stannate.

Aniline obtained in the experiment is clouded by water emulsified in it. Solid sodium hydroxide is commonly used to bind water emulsified and dissolved in aniline. Do not use calcium chloride to dehydrate aniline since it reacts to form $CaCl_2 \cdot 2C_6H_5NH_2$.

Pure aniline is a colourless oily liquid with a characteristic odour; it rapidly becomes brown on exposure to air; it is only sparingly soluble in water (about 3.5 : 100 at 20 °C and 6 : 100 at 100 °C) and is volatile with steam (see Experiment 6). It can be salted out from its aqueous solution with common salt (cf. Experiments 38, 95, and 100). Aniline dissolves about 5 per cent by weight of water at room temperature.

Aniline vigorously reacts with fuming nitric acid to give a large volume of gaseous products. This reaction (oxidation of aniline) is used in jet-plane and rocket engines.

The industrial method of manufacturing aniline is based on the catalytic reduction of nitrobenzene by gaseous hydrogen.

203
Formation and Decomposition of Aniline Salt

REAGENTS

Aniline (prepared in the previous experiment).

Shake 6-8 drops of aniline with 2-3 ml of water to prepare an emulsion. Divide the emulsion into two parts.

Add concentrated hydrochloric acid, drop by drop and with shaking, to one part of the emulsion until a homogeneous solution is obtained. Add two drops of phenolphthalein and then alkali solution, drop by drop: the liquid becomes clouded by the aniline long before the colour of phenolphthalein changes to indicate alkalinity.

Add dilute sulphuric acid, also drop by drop, to the remaining part of the emulsion: crystalline substance precipitates.

Like all amines, aniline is a base. But the effect of aromatic nucleus, connected directly with the amino group, shows itself in the marked weakening of the basic properties in aromatic amines compared with those of the fatty amines. The orbital of the free pair of *p*-electrons of the nitrogen atom is overlapped by the π-electrons of the aromatic nucleus. The nitrogen atom gains a partial positive charge and the attack of the proton is made difficult. A similar effect produced by the benzene ring is manifested by the stronger acid properties of phenols compared with alcohols (see Experiment 165). This effect is marked only in cases where the benzene ring is connected directly with the amino group or hydroxyl. For example, benzylamine, $C_6H_5CH_2NH_2$, and benzyl alcohol, $C_6H_5CH_2OH$, stand closer to fatty amines and alcohols as regard their properties.

Aniline reacts with mineral acids to form stable crystalline salts; aniline hydrochloride, $[C_6H_5NH_3]Cl$, can be distilled without decomposition. Most aniline salts are readily soluble in water; the sulphate, $[C_6H_5NH_3]_2SO_4$, is less soluble.

Aniline is a much weaker base than, for instance, ammonia. Its ionization constant is only 4×10^{-10}. Aniline salts are therefore strongly ionized in aqueous solutions and react clearly acid.

In 1897, N. A. Menshutkin established that the salts of aromatic amines can be titrated with alkali (like free acids) using phenolphthalein as indicator.

204
Bromination of Aniline

REAGENTS

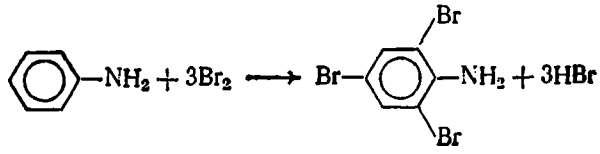
Antiline, dilute solution.

Add a small drop of aniline to 5-6 ml of water and shake to dissolve it. Use this very dilute solution also in Experiment 205.

Add bromine water, drop by drop, to 1 ml of aniline solution: the bromine colour vanishes and cloudiness appears.

Incorporation of the amino group into the aromatic ring, as well as of the hydroxyl group, sharply increases the mobility of hydrogen atoms at the carbon atoms of the benzene ring (see Experiments

166 and 167, and explanations to them). Aniline is therefore easy to brominate even in dilute solutions. A sparingly soluble 2,4,6-tribromoaniline (m.p. 119 °C) is formed in the reaction:



Bromination of aniline weakens even more its basic properties, and tribromoaniline is almost insoluble in dilute acids.

Aniline salts are brominated like aniline itself.

205
Oxidation of Aniline

REAGENTS

Aniline, dilute solution (see Experiment 204).
Calcium hypochlorite, or *sodium hypochlorite*, solution.
Sodium hypobromite, solution.
Potassium dichromate, saturated solution.

To prepare calcium hypochlorite solution, shake a small quantity of bleaching powder (chlorinated lime) with 10-20 volumes of water and pass the liquid through a pleated filter. To prepare sodium hypochlorite solution, add dilute sodium hydroxide solution to chlorine water until chlorine odour is no longer felt. Sodium hypobromite should be prepared in a similar way, by adding alkali solution to bromine water until the solution is colourless.

A. Place 1 ml of aniline water into two separate test tubes, add a few drops of hypochlorite to one and of hypobromite to the other test tube: the liquid in the former turns red and soon changes to deep violet, whereas in the latter a bright red colour first develops and then a precipitate falls out.

B. Add 2-3 drops of potassium dichromate and 0.5 ml of dilute sulphuric acid to 1 ml of aniline water: the liquid turns dark green, then dark blue, and finally black.

The colour reactions of aniline oxidation are very sensitive (especially with hypochlorite) and specific. They are quite reliable with strongly dilute aniline solutions as well. Aniline is very easily oxidized to form (depending on the oxidation conditions and the nature of the oxidant) various substances, e.g. azobenzene, azoxybenzene, nitrobenzene, nitrosobenzene, benzoquinone, etc.

In the conditions of our experiment, aniline is oxidized to give complicate coloured compounds containing the quinoid group =⟨⟩=. The product of aniline oxidation with dichromate, *aniline black*, is very stable to acids and alkalis, and is often used to dye fibres and to paint laboratory tables. The salts of aniline give with hypochlorite somewhat different colours.

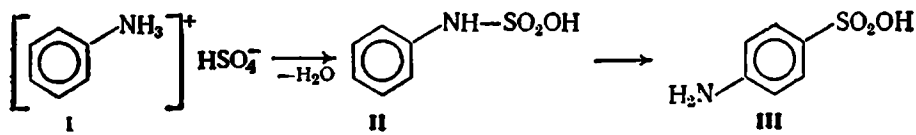
206
Preparing Sulphanilic Acid

REAGENTS

Aniline.

Pipette 2 ml of aniline into a test tube taking care as not to wet the walls. Add, by small portions and with shaking, 2.5 ml of concentrated sulphuric acid. The mixture first solidifies, and then thins. Immerse the test tube (below the mixture level) into a small sand bath, heat to 180-190 °C (thermometer in the mixture) for 20-25 minutes, then remove, pull out the thermometer, allow the mixture to cool until it begins to solidify, and add 10 ml of hot water. Heat the mixture again until the precipitate is all dissolved, and allow the solution to cool slowly, preferably to 0 °C. Separate the precipitated crystals of sulphanilic acid on a filter with suction and press out excess liquid. The yield is 1.7-1.8 g.

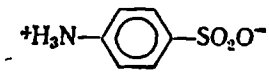
Like phenols (see Experiment 171), aromatic amines are sulphona ted easier than the corresponding hydrocarbons. When mixed with sulphuric acid, aniline first gives acid sulphate (I). As it is heated, water is eliminated and phenylsulphamic acid (II) is formed. Further heating causes intramolecular rearrangement and transition of the sulpho group into the nucleus. At a temperature of 180 °C and above, sulphanilic acid(III) is predominantly obtained; at lower temperatures the ortho isomer is also formed



I II III

Clystalline sulphanilic acid contains two molecules of water of crystallization that is gradually lost on drying. The acid is very sparingly soluble in cold water: 1 g in 166 ml at 10 °C. It is well ionized in aqueous solutions ($K = 6 \times 10^{-4}$) and is stronger than benzoic acid (see Experiment 184). The amino group does not impart appreciable basic properties to sulphanilic acid; it is easily diazotized.

Free sulphanilic acid presumably has the structure of the inner salt, i.e. of a dipolar ion:



207
Preparing Acetanilide

REAGENTS

Aniline.
Acetyl chloride.
Acetic anhydride.

A. Place 1 ml of aniline in a test tube. Very carefully and with shaking and cooling by water, add 1 ml of acetyl chloride, drop by drop. Add 10 ml of water to the obtained mixture and shake strongly: crystals of acetanilide precipitate. To accelerate the crystallization, rub the walls of the test tube with a glass rod. (The tube walls should be wetted.) The other reaction product, aniline hydrochloride, remains in solution.

B. Place 1 ml of aniline and 3 ml of water into a test tube, stopper it, and strongly shake to prepare emulsion. Add 1 ml of acetic anhydride and shake again, first carefully and then strongly. Acetanilide crystallizes, and the mixture solidifies into a thick mass.

Acetanilide obtained in tests A and B can be re-crystallized (see Experiment 2). The yield is about 1 g.

C. Boil a small amount of acetanilide with alkali and observe the reaction.

208
Preparing Benzanilide

REAGENTS

Aniltne.
Benzoyl chloride.

Place 0.5 ml of aniline, 1 ml of benzoyl chloride, and 5 ml of concentrated alkali solution into a test tube. Shake the mixture first carefully, with cooling the test tube in cold water, and then strongly (stopper the test tube) until the odour of benzoyl chloride is felt no longer. Ample quantities of benzanilide and sodium benzoate are crystallized. Add 3-5 ml of water and shake the mixture again: sodium benzoate dissolves.

White, or slightly brownish benzanilide can be purified by washing with water and dilute hydrochloric acid on a filter and then re-crystallized from ethyl alcohol. The yield is about 1 g.

Primary and secondary amines react with acid chlorides like ammonia (cf. Experiment 193). Aniline has a free electron pair at the nitrogen atom and, like a nucleophile, attacks the carbon atom of the carbonyl group of acid chloride or anhydride (see explanations to Experiment 96); chloride or acetate ions are then eliminated.

Aniline is acetylated on prolonged boiling with glacial acetic acid. Acetylation of aniline with acetyl chloride or acetic anhydride is a faster process.

Hydrogen chloride that is liberated in the reaction of aniline with acetyl chloride is bound with aniline excess, and the summary reaction can be expressed by the following equation:

$$CH_3COCl + 2C_6H_5NH_2 \longrightarrow CH_3CONHC_6H_5 + [C_6H_5NH_3]^+Cl^-$$

The entire aniline can be involved in the reaction with acid chloride in the presence of alkali or pyridine (see below).

Amines are acetylated by only one acid radical of acetic anhydride, whereas its other radical gives acetic acid:

$$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH$$

Acetic acid binds aniline insufficiently strongly, and the latter fully takes part in the acetylation reaction.

Like acid amides non-substituted at the nitrogen (see Experiments 113 and 118), acetanilide is stable to water, but when boiled with acids or alkalis, it is hydrolysed to give aniline and acetic acid.

In conditions of Experiment 208, the reaction proceeds as follows:

$$C_6H_5NH_2 + ClCOC_6H_5 \longrightarrow C_6H_5NHCOC_6H_5 + HCl$$

In an alkaline medium, hydrogen chloride is bound, the amine fully enters into the reaction, and the benzoylation process occurs rapidly (cf. Experiments 196 and 207). Benzanilide melts at 160 °C.

Tertiary amines have no hydrogen at the nitrogen atom and either do not react with acid chlorides, or form addition products of the ammonia salt type. Similarly, tertiary amines bind hydrogen chloride. Some of them, for instance pyridine (see Experiment 241), are therefore used in reactions of acid chlorides with alcohols, phenols, primary and secondary amines, instead of alkali. The advantage of pyridine over aqueous alkali is that it dissolves both starting substances, and the reaction of acylation proceeds in a homogeneous medium.

209
Formation of Isonitrile

REAGENTS

Aniline.
Ethyl alcohol.
Chloroform.

Use the HOOD. Check it before the experiment.

Place a drop of aniline, 2-3 drops of concentrated alkali solution, 2 drops of chloroform, and 0.5-1 ml of alcohol in a test tube and heat the mixture slowly to boiling: the specific, very unpleasant odour of isonitrile appears.

On the termination of the experiment, place the test tube into a bath containing dilute sulphuric or hydrochloric acid to destroy isonitrile. Perform this operation in the hood.

Formation of isonitriles by the action of alkali on chloroform in an alcohol solution is characteristic of primary amines, both fatty (see Experiment 114) and aromatic. Only few primary amines, e.g. naphthalene and anthracene derivatives, do not give this reaction.

210
Diazotization of Aniline

REAGENTS

Aniline.
Sodium nitrite.
Starch-iodine paper.

To prepare the test paper, dilute a freshly boiled starch solution (see Experiment 137) with 4-5 volumes of boiling water, cool, dissolve potassium iodide in the solution (0.1-0.2 g per 100 ml), and finally impregnate filter paper in this solution. Dry the paper and cut it into strips. Keep them in a well stoppered bottle.

Mix 3 g of aniline with 25 ml of water and 7 ml of concentrated hydrochloric acid in a 50-100 ml flask. Cool the obtained clear solution of aniline hydrochloride in dilute hydrochloric acid to 0 °C in a mixture of water and snow or crushed ice.

Dissolve 2.3 g of sodium nitrite in 4-5 ml of water in a separate test tube and slowly add this solution, with cooling, to the cooled aniline solution. Add it dropwise, with shaking and cooling. The temperature of the mixture should never rise above 5-7 °C. To attain this, drop small pieces of ice or snow into the flask from time to time. (The amount of ice or snow added should not exceed 12 g.) Despite the strongly acid reaction, nitrogen oxides (the products of

decomposition of free nitrous acid) are not evolved from the mixture. When about half the required quantity of sodium nitrite solution has been added (in about 5-6 minutes), shake the mixture for 1-2 minutes and, using the thermometer, place a drop of the solution onto the test paper. If the colour of the paper does not change, add more sodium nitrite and repeat the test with the paper. Development of blue or brown colour indicates appearance in the mixture of free nitrous acid. Shake the mixture and repeat the test with the paper. If it shows that nitrous acid has entered into the reaction and is absent in the free state, continue adding sodium nitrite.

Discontinue the diazotization when free nitrous acid is again detected in the mixture and remains there after shaking for a few minutes. This usually happens when almost the entire amount of sodium nitrite has been added.

Keep the flask containing almost fully clear solution of phenyldiazonium salt on ice and use it in further experiments (Experiments 211 and 212).

The reaction of diazotization (formation of diazo compounds by the action of nitrous acid) is characteristic of primary aromatic amines. The reaction occurs in an acid medium, which is necessary to liberate free nitrous acid from its salt.

Aromatic amines react with mineral acids to give salts (cf. Experiment 203) that are similar to those of ammonium. Nitrous acid reacts with cation of amine salt to eliminate water and to form diazonium salt, whose complex cation contains two nitrogen atoms:

$$ArNH_2 \xrightarrow{HCl} [ArNH_3]^+Cl^- \xrightarrow{HONO} [ArN_2]^+Cl^- + 2H_2O$$

It has been shown recently that a molecule of free amine (the product of hydrolysis of its salt) and a hydrogen ion of the medium react with free nitrous acid, whereas nitrous acid itself reacts in the form of more active entities (which are formed from the acid in an acid medium), namely, nitrosacidium, $H_2NO_2^+$, nitrosonium, NO^+, or (in the presence of hydrochloric acid) molecules of nitrosyl chloride NOCl (see also explanations to Experiment 220).

The diazonium salt is an analogue to the salt of tetrasubstituted ammonium (see explanations to Experiment 110), in which another nitrogen atom stands in place of three hydrocarbon radicals at the nitrogen atom. The diazonium salt can thus be regarded as a derivative of the nitrogen molecule whose one atom becomes a donor of the electron pair (like the ammonia nitrogen).

Diazonium salts of strong acids are colourless, usually readily soluble in water; unlike salts of weak bases (e.g. original aromatic amines), they almost do not hydrolyse in aqueous solution, and their solutions react neutral. Diazonium salts are unstable; when

dry they are explosive (cf. Experiment 213), and in solution form they are quite reactive.

Alkalis act on diazonium salt to give a strong base, diazonium hydroxide, which rearranges into diazo hydrate in an alkaline medium:

$$[ArN_2]^+Cl^- \underset{HCl}{\overset{NaOH}{\rightleftharpoons}} [ArN_2]^+OH^- \rightleftharpoons Ar-N=N-OH$$

The other, tervalent, nitrogen atom of the diazonium group that bears a partial positive charge produced by the attraction of the electron pair of the bond to the first nitrogen atom, undergoes a nucleophilic attack of the HO^- ion.

Diazo hydrates are weak acids and react with alkali to give salts, diazotates, $ArN=N-ONa$, which are strongly hydrolysed in solution and decompose with liberation of nitrogen. The salts are readily coupled to give azo compounds.

In the presence of an excess of a strong acid, the conversions are reversed: diazotate converts into diazo hydrate, which is rearranged into diazonium hydroxide, and the latter reacts with acid to give salt.

Diazo hydrate can be formed by the action of nitrous acid on free aromatic amine.

It was considered earlier that diazo hydrates and diazotates exist in two stereoisomeric forms: *cis* and *trans*, or *syn* and *anti* isomers. But in 1959, B. A. Porai-Koshits showed that these substances are formed in one form only.

During the diazotization process the reaction mixture should be carefully cooled to retard the decomposition of nitrous acid (and its withdrawal from the reaction sphere) and also decomposition of diazo compound by water (see Experiment 211). Nitrous acid reacts with amine in time because the reaction is not ionic. The diazotization should therefore be carried out slowly to prevent accumulation of free nitrous acid. The decomposition of the acid with the formation of nitrogen oxides accounts for the presence of excess amine salt in the reaction mixture. The salt (especially in the deficit of a mineral acid) can bind diazo compound to condense with it (see Experiment 216).

The presence in the mixture of free nitrous acid can be detected by the starch-iodine test paper, which becomes coloured by the iodine liberated from potassium iodide in an acid medium (cf. Experiment 54).

Diazotization of primary aromatic amines is an important industrial process since a great variety of conversions of diazo compounds is used for preparing various organic products, such as dyes, medicines, etc. This method was developed by Griess in 1858.

Primary fatty amines react with nitrous acid to give first diazo hydrates (like aromatic amines), but the diazo compounds of the fatty series are unstable and immediately decompose to liberate nitrogen:

$$RNH_2 + O{=}N{-}OH \longrightarrow RN{=}N{-}OH + H_2O$$
$$RN{=}N{-}OH \longrightarrow ROH + N_2$$

Thus, the product of reaction of fatty amine with nitrous acid is alcohol (cf. Experiment 117). Fatty diazo compounds are therefore produced by other methods. But, for instance, glycine ethers, containing the $-OCOCH_2NH_2$ grouping, are diazotized like aromatic amines.

Secondary amines react with nitrous acid to give N-nitrosamines, $R_2N{-}NO$ (see Experiment 218). Tertiary amines react with nitrous acid to give only salts (like primary and secondary amines) that are usually unstable. Tertiary aromatic amines can react with acid at the expense of hydrogen atoms of the aromatic ring (cf. Experiment 219).

211
Formation of Phenol (Substitution of Hydroxyl for Diazo Group)

REAGENTS

Phenyl diazonium salt, solution (see Experiment 210).

Place 5-10 ml of cold solution of phenyl diazonium salt in a test tube, close it with a stopper with a glass outlet tube, and fix in the stand in the inclined position. Heat the liquid slowly in hot water in a beaker. The solution turns cloudy and much gas is evolved. Pull a piece of rubber tubing onto the outlet tube and pass the gas into a dish or a beaker containing alkali solution and a small quantity of potassium permanganate.

Collect the gas over the liquid into an overturned test tube. Make sure that the evolving gas is odourless, is not absorbed in the alkali solution, is neither flammable, nor maintains burning.

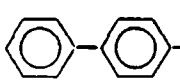
The liberation of gas stops in a few minutes and a black oily drop is formed over the cloudy liquid in the test tube. Now remove the rubber tubing, put away the water bath, wipe dry the test tube, add a boiling stone, and begin distillation by carefully heating first the upper layers of the liquid over a burner. Immerse another test tube in cold water in a beaker and use it as a receptacle. Discontinue the distillation when 1-2 ml of emulsion, having a characteristic odour, are collected in the receptacle.

Dilute the distillate with several volumes of water. It gives all reactions characteristic of phenol (see Experiments 167, 168, and 175).

Diazonium salts react with water at room temperature. The reaction is faster with heating. In this case the diazo group is eliminated in the form of a molecular nitrogen and is replaced by the hydroxyl. Phenyl diazonium hydrochloride gives phenol:

$$[C_6H_5N_2]^+Cl^- + H_2O \longrightarrow C_6H_5OH + HCl + N_2$$

During distillation phenol passes into the receptacle together with steam at a temperature of about 100 °C, i.e. at a temperature that is much lower than that at which it boils (cf. Experiment 6).

Part of phenol reacts with the diazo compound to give a side product, *p*-phenylphenol  (m.p. 164 °C), which is almost non-volatile with steam.

The high reactivity of diazo compounds makes it possible to substitute not only hydroxyl but also hydrogen, chlorine, bromine, iodine, cyano group, etc. for the amino group in the benzene ring.

Nitrogen liberated in the experiment can contain admixtures of its oxides, NO and NO_2, that are formed by decomposing excess nitrous acid. These admixtures are bound with alkaline solution of potassium permanganate.

212
Formation of Azo Dyes

REAGENTS

Phenyl diazonium salt, solution (see Experiment 210).
Dimethylaniline.
Phenol.
β-*Naphthol.*
Sodium acetate, saturated solution.
White cotton fabric (Test C).

A. Place 1-2 ml of water in a test tube, add 3-5 drops of dimethylaniline, and dissolve it with concentrated hydrochloric acid, adding it drop by drop, with shaking. Cool the obtained clear solution in cold water, add 2-3 ml of phenyl diazonium chloride solution, then 1-2 ml of sodium acetate solution, and shake the mixture; brownish-yellow flakes of dimethylaminoazobenzene precipitate.

Mix a few drops of the suspension in another test tube with 5-7 ml of water: a yellow solution turns red on acidification. When alkalized, it again turns yellow.

B. Prepare separately solutions of small amounts (0.1-0.2 g) of phenol and β-naphthol in 2-3 ml of dilute alkali solution. Divide the solutions into two parts. Keep one part of each solution for

Test C. Add about an equal volume of phenyl diazonium salt solution to the remaining parts: an intense orange colour develops immediately. The mixture containing beta-naphthol also gives ample orange precipitate that can be separated on a filter with suction and dried.

C. Dilute the remaining (Test B) alkaline solutions of phenol and naphthol with 3-5 volumes of water and dip strips of white cotton fabric in the liquids for a few minutes.

Meanwhile, transfer 5-10 ml of the cold phenyl diazonium solution into another test tube or a beaker and add 1-2 pieces of ice and 1-2 ml of sodium acetate solution.

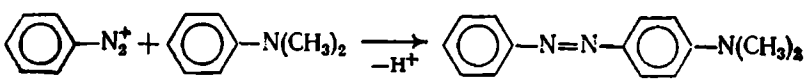
Remove the cotton strips from the solutions, press them slightly, and dip in the prepared diazonium salt solution: the strips turn bright orange immediately. In 5-6 minutes, remove the strips, rinse them well in water, and dry. Note that the dye almost does not pass into the washings

The reaction of diazo compound with aromatic amine or phenol (without liberation of nitrogen that gives the atom grouping Ar—N= =N—Ar) is known as the coupling reaction of diazo compound. This is the electrophilic substitution reaction in which the electrophile is the cation of the diazonium salt. The products of the coupling reaction, azo compounds, are quite stable and are usually brightly coloured. Many of them are dyes, that is, they have affinity for fibres.

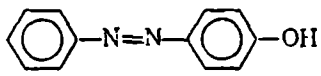
Coupling with phenols is usually effected in an alkaline medium, and that with amines, in a weak acid medium (excess mineral acid is destroyed by adding acetate). If the acidity of the medium is too high, amine converts into an ammonium salt, and the formation of phenolate ion from phenol becomes less feasible. The mobility of the hydrogen atoms of the aromatic ring sharply decreases in both cases. In other words, the reaction of coupling becomes more difficult to realize. The optimum acidity (pH) for the coupling reaction depends on the nature of the reacting components.

Phenols and aromatic amines contain quite mobile hydrogen atoms at the carbon atoms of the benzene nucleus (see Chapter 13). In the coupling reaction, the azo group is substituted for one of these hydrogen atoms (as a rule, for the hydrogen atom in the position para or ortho to the phenol hydroxyl or to the amino group of the amine).

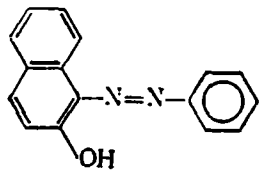
Dimethylaniline is coupled with phenyl diazonium to form *p*-dimethylaminoazobenzene:



Coupling of phenol gives *p*-hydroxyazobenzene:

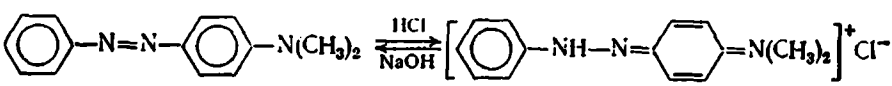


and beta-naphthol gives benzeneazo-beta-naphthol (Sudan-I):



The colour of azo compounds depends on the chromophoric group, in our case the azo group Ar—N=N—Ar. In order to ensure better affinity for the fibres, the azo dye molecule should also contain other atom groupings, either of acid (—OH, $-SO_2OH$) or basic (amino group) character. Acid and basic dyes are distinguished accordingly. Acid and basic groups usually affect the shade of the colour, and during the dying process, they permit the formation of stable salt-like compounds from the dye and amphoteric proteins of wool or silk (Experiment 275). Vegetable fibres, such as cotton or flax, consisting of cellulose, retain the azo dye mainly on account of the adsorption on their surfaces. Hence the weaker colour fastness.

If the aqueous solution of dimethylaminoazobenzene is acidified (Experiment 212, test A), a salt of this tertiary amine is formed. The proton is attached to the azo group, the molecule structure changes, and the structure of the cation becomes quinonoid. The yellow solution turns red, but as the acid solution is alkalized, the yellow colour is restored:



Similar ring-substituted azo compounds, such as methyl orange (Experiment 214), sharply change their colour in these conditions and can therefore be used as indicators that permit drawing judgement on the acidity of solution by the change of colour.

213
Diazotization of Sulphanilic Acid

REAGENTS

Sulphanilic acid (see Experiment 206).
Sodium nitrite.

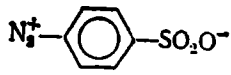
Dissolve 1.5 g of sulphanilic acid and 0.75 g of sodium nitrite in a few millilitres of dilute alkali solution. Add the obtained solution to a mixture of 1.5 ml of concentrated sulphuric acid and 20 g of ice or snow with stirring in a small beaker. Diazobenzenesulphonic acid precipitates immediately.

Allow the mixture to stand for 10-15 minutes and separate the precipitate with suction. Keep it moist for Experiment 214.

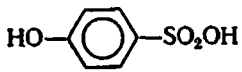
Mix a small quantity of diazobenzenesulphonic acid with 5-7 ml of water. Transfer part of this mixture into another test tube, and heat the remaining part to boiling: ample quantities of nitrogen are liberated, and the diazobenzenesulphonic acid precipitate is all dissolved. Heat the solution for 5-10 minutes, cool the yellow liquid, and add a few drops of ferric chloride solution. Add the same quantity of ferric chloride to the part of the solution that was not heated. Compare the colour in both test tubes.

Put the remaining acid, which will not be used in Experiment 214, into the sink and wash off with a strong jet of water.

As the alkaline solution of sulphanilic acid is acidified, it is diazotized by nitrous acid that is liberated in the reaction, and diazobenzenesulphonic acid is precipitated. The structure of the new acid is as follows:



The acid is sparingly soluble in cold water. If the mixture in water is heated to 60 °C and over, the acid first dissolves but then decomposes; the diazo group is replaced by the hydroxyl (cf. Experiment 211) in this process. The formed phenol-*p*-sulphonic acid



is readily soluble in water; like most phenols it reacts with ferric chloride to give a complex salt (cf. Experiment 168). The solution of the salt is deep violet.

Like all diazo compounds, dry diazobenzenesulphonic acid is very unstable and *decomposes with explosion even on friction.* Therefore, do not dry the acid, nor keep it. Moist acid is safe.

214
Preparing Methyl Orange (Helianthine)

REAGENTS

Diazobenzenesulphonic acid (Experiment 213).
Dimethylaniline.

Mix 0.75 ml of dimethylaniline and a few drops of concentrated acetic acid in a wide test tube or a small beaker to prepare a clear solution of amine acetate. Add a few pieces of ice to the solution. Now mix the moist diazobenzenesulphonic acid obtained in Experiment 213 with 2-3 ml of water and add it with stirring to the ice-cold solution. Add 1-2 ml of concentrated alkali solution to the mixture until it reacts strongly alkaline to litmus: an orange sodium salt of the dye precipitates. Allow the mixture to stand for 15-20 minutes and separate the salt with suction. Dry the precipitate.

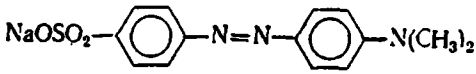
The yield is about 1.5 g. The product can be re-crystallized from a few millilitres of hot water.

Put a small amount of the remaining solution into a test tube, dilute it strongly with water, and observe the change of colour as acid and then alkali are added.

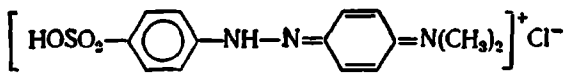
Methyl orange can also be prepared from dimethylaniline and the mixture containing the diazo compound obtained in Experiment 213. The yield is slightly lower.

Methyl orange can be used in Experiment 215.

Diazobenzenesulphonic acid couples in an alkaline solution (cf. Experiment 212) with dimethylaniline to give *p*-dimethylaminoazobenzenesulphonic acid, whose sodium salt is sparingly soluble in cold water. The salt is known as methyl orange or helianthine:



Methyl orange is a common acid-base indicator. In a slightly acid medium the yellow colour of its alkaline or neutral solution changes to red because of the formation of the salt having the quinonoid structure:



At higher concentration of the dye, it precipitates.

215
Reduction of Azo Dye

REAGENTS

Methyl orange (Experiment 214).
Stannous chloride, solution.
Potassium dichromate, saturated solution.
Dimethylaniline.
Ethyl ether.

Prepare stannous chloride solution by mixing 1 g of solid $SnCl_2 \cdot 2H_2O$ and 2-3 ml of concentrated hydrochloric acid with slightly heating.

Place 0.2-0.3 g of methyl orange in a test tube, add 2-3 ml of water, and heat to boiling to dissolve the dye. Add stannous chloride solution dropwise to destroy the red colour. Cool the yellowish solution in water, allow it to stand for 10-15 minutes, and separate the precipitated crystals of sulphanilic acid on a filter with suction.

Add concentrated alkali solution to the filtrate to dissolve tin hydroxides that first precipitate. Cool the obtained alkaline liquid, shake strongly (stopper the test tube) with 2-3 ml of ether, and allow to stand. Using a pipette, transfer the greater part of the ether layer into a dish or onto a watch glass. The ether vaporizes and crystals of *p*-aminodimethylaniline remain on the glass. The substance is characterized by the following tests.

A. Mix a small amount of the ether diamine solution with 1 ml of water, add a drop of dilute acetic acid and a small drop of potassium dichromate solution: intense red colour develops. In the presence of excess $K_2Cr_2O_7$ the solution turns dark brown.

B. Mix 0.5 ml of the ether diamine solution with 1-2 ml of water, add a drop of dimethylaniline, a drop of concentrated hydrochloric acid, and cool the mixture. Now add a small drop of potassium dichromate: the mixture turns bright green.

The colour of both solutions persists in strongly diluted solutions as well.

Stannous chloride is a strong reductant in an acid medium:

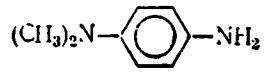
$$Sn^{2+} + 2H^+ \longrightarrow Sn^{4+} + 2H$$

Stannous chloride or other similar reagents (zinc and sulphuric acid, sodium hydrosulphite $Na_2S_2O_4$, see Experiment 246) easily reduce the azo dye with splitting the molecule. The dye is reduced at the double bond of the azo group —N=N—, which breaks down to give two amino groups:

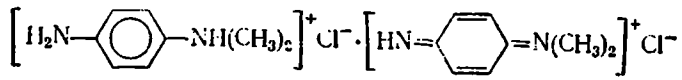
$$R-N=N-R' \xrightarrow{4H} RNH_2 + NH_2R'$$

The resultant product is the original aromatic amine that was diazotized into the azo dye. The component that was coupled with the diazo compound is obtained in the form of the amino derivative. The reduced products are therefore indicative of the structure of the azo dye and can suggest the way by which the dye was prepared.

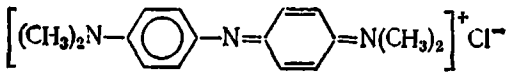
The reduction of methyl orange gives sulphanilic acid and N,N-dimethyl-*p*-phenylenediamine (*p*-aminodimethylaniline):



The obtained diamine (m.p. 41 °C) is very reactive. It oxidizes to give a red complex compound having, like quinhydrone, a quinonoid structure (see Experiment 226):



The oxidation in the presence of dimethylaniline gives another compound, also having the quanonoid structure:



The compound is green.

216
Formation of Diazoaminobenzene and Its Reactions

REAGENTS

Phenyldiazonium salt, solution (see Experiment 210).
Sodium acetate, 20 per cent solution.
Aniline.

Place a few millilitres of cold phenyl diazonium salt solution into a test tube, add 2-3 drops of aniline, and if it does not dissolve, add 1-2 drops of hydrochloric acid. Cool the mixture in snow and add an equal volume of sodium acetate solution. Separate the precipitated yellow diazoaminobenzene on a filter with suction and use it in the following tests.

A. Heat a part of the obtained product in a test tube with 2-3 ml of dilute hydrochloric acid: nitrogen is liberated. The odour betrays the formation of phenol.

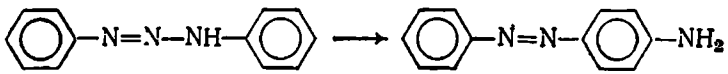
B. Gently heat the remaining part of diazoaminobenzene in a test tube with 3-4 drops of aniline for 2-3 minutes, then add 5-7 ml of dilute hydrochloric acid: an intense colour develops.

Primary amines react with diazo compounds in a weakly acid medium on account of the hydrogen atoms belonging not to the benzene ring (as is the case with phenols and tertiary amines) but to the amino group (see Experiment 212 and explanations to it). Diazoaminobenzene is formed in the conditions of our experiment:

$$C_6H_5-N=NOH+NH_2-C_6H_5 \xrightarrow[-H_2O]{} C_6H_5-N=N-NH-C_6H_5$$

It precipitates as yellow crystals melting at 98 °C (after re-crystallization from ethyl alcohol) or quickly solidifying oil.

If the diazotization process is effected in the deficit of nitrous acid, part of amine remains free, and the products of diazo compounds in other reactions (see Experiments 211 and 212) are contaminated with diazoaminobenzene. When heated in an acid medium, diazoaminobenzene falls into the amine salt and the salt of diazonium. The latter converts into phenol to liberate nitrogen (Experiment 211). When heated in an acid medium in the presence of excess aniline, diazoaminobenzene gives *p*-aminoazobenzene:



The substance is also the product of the reaction of diazonium salt, which is formed in the process, with the amine.

Aminoazobenzene (m.p. 127 °C) has the structure that accounts for its intense colour (cf. Experiment 212). The substance is a true azo dye, though unstable.

217
Formation of Diphenylamine Salt and Its Hydrolysis

REAGENTS

Diphenylamine.
Ethyl alcohol.

Dissolve a few crystals of diphenylamine in 0.5-1 ml of alcohol. Slowly add 2-3 ml of water: white cloudiness develops. Add concentrated hydrochloric acid drop by drop: the amine dissolves again. Add water to the acid solution: the precipitate re-appears.

Diphenylamine, containing two phenyl groups at the nitrogen atom, is a base that is weaker than aniline (see Experiment 203). A well soluble hydrochloride of diphenylamine is therefore formed only in the presence of a great excess of the acid, which shifts the equilibrium to the right:

$$(C_6H_5)_2NH + HCl \rightleftharpoons [(C_6H_5)_2NH_2]^+Cl^-$$

In the presence of excess water, the salt is hydrolysed, i.e. the equilibrium of the reaction is shifted to the left. For the same reason, the solution of diphenylamine in concentrated sulphuric acid, which is used as a reagent for nitrous and nitric acids, develops turbidity on dilution with water.

218
Preparing N-Nitrosodiphenylamine

REAGENTS

Diphenylamine.
Ethyl alcohol.
Sodium nitrite.

Dissolve 1 g of diphenylamine in 5-6 ml of alcohol and cool the solution to 0 °C in a mixture of ice (snow) and water. If crystals of diphenylamine precipitate on cooling, dissolve them by adding 1-2 ml of alcohol. Continue the cooling, add with shaking, first 0.9 ml of concentrated hydrochloric acid and then 0.5 g of sodium nitrite solution in 1 ml of water.

On addition of the acid the mixture remains clear, but as sodium nitrite is added, it turns yellowish-green and cloudy. The heavy oil that is formed in this reaction quickly solidifies on subsequent shaking and cooling. Allow the mixture to stand for 5-10 minutes and separate the obtained yellowish crystals of nitrosamine on a filter with suction. Wash them with a few drops of alcohol, then with water, and press out excess liquid. The obtained product (about 0.8-1 g) can be used in Experiment 221.

N-Nitrosodiphenylamine melts at 66 °C (after re-crystallization from alcohol).

Secondary fatty and aromatic amines react with nitrous acid to give N-nitrosamines according to the general equation:

$$\begin{matrix} R \\ \diagdown \\ \diagup \\ R \end{matrix}\!\!>\!NH + HO-N=O \longrightarrow \begin{matrix} R \\ \diagdown \\ \diagup \\ R \end{matrix}\!\!>\!N-NO + H_2O$$

Concentrated mineral acids easily eliminate the nitroso group from nitrosamines to form nitrogen oxides and the salt of the original

amine. Nitrous acid reacts with diphenylamine without intense cooling and in the presence of excess hydrochloric or sulphuric acid to oxidize it by the liberated nitrogen oxides and to colour the mixture blue (see Experiment 221).

219
Preparing para-Nitrosodimethylaniline

REAGENTS

Dimethylaniline.
Sodium nitrite.
Ethyl ether.

A. Place 1 g of dimethylaniline in a wide test tube and add 2 ml of concentrated hydrochloric acid. Mix the components and cool the test tube in ice-cold water. Add 8 g of crushed ice. Very slowly, within 5-10 minutes, add a solution of 0.6 g of sodium nitrite in 2 ml of water. After adding each next small portion, close the test tube with a stopper, shake strongly, and cool in ice-cold water. The mixture turns brown, and yellow crystals of *p*-nitrosodimethylaniline hydrochloride precipitate. As soon as sodium nitrite is all added, allow the mixture to stand for 15-20 minutes in an ice-cold bath, then separate the crystals on a filter with suction and press out excess liquid in filter paper.

Use the obtained product (1-1.2 g) for isolation of free amine in Test B, and also in Experiments 221 and 222.

B. To isolate free *p*-nitrosodimethylaniline, place about a quarter or a third of the obtained salt in a test tube and add, drop by drop, with shaking, 3-4 ml of soda solution: a green precipitate falls out. Add 2 ml of ether and shake: the crystals dissolve.

Using a pipette, transfer the ether layer into a dry test tube, and extract the aqueous solution three times with 2-ml portions of ether, strongly shaking the mixture. Collect the ether extracts in one test tube and allow to stand: a drop of water solution usually separates from the extract. Decant the ether extract into a porcelain or a glass dish and evaporate the ether at room temperature in the HOOD. Bright green crystals of *p*-nitrosodimethylaniline remain in the dish.

220
Preparing para-Nitrosophenol

REAGENTS

Phenol.
Sodium nitrite.

Mix 0.5 g of phenol, 0.4 g of sodium nitrite, 0.5-0.6 ml of concentrated alkali solution, and 5 ml of water in a test tube, and cool

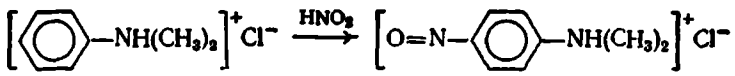
the mixture to 0 °C on an ice-cold bath. Weigh out 7 g of crushed ice into a bigger test tube and add 0.7 ml of concentrated sulphuric acid. Very slowly and with constant cooling to 0 °C and shaking, add the alkaline solution of phenol and sodium nitrite.

Allow the dark liquid containing a precipitate to stand at 0 °C for 15-20 minutes, then separate the precipitate with suction, wash several times with a few drops of ice-cold water, and press out excess liquid. The yield is 0.3-0.4 g.

Use the obtained *p*-nitrosophenol in Experiment 221.

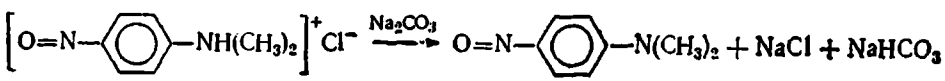
Unlike primary (see Experiment 210) or secondary (Experiment 218) amines, tertiary amines usually do not react with nitrous acid. But if the molecule of a tertiary amine contains an aromatic ring with a free hydrogen atom in the position para to the amine nitrogen atom, this hydrogen atom is easily replaced by the nitroso group —N=O by the action of nitrous acid. The presence of other substitutes in this ring often makes the nitrosation reaction hardly feasible.

Dimethylaniline reacts with nitrous acid in a hydrochloric acid medium to give *p*-nitrosodimethylaniline hydrochloride:



The melting point of the salt, washed with several drops of alcohol is 175-177 °C.

By the action of soda, this salt can be converted into free *p*-nitrosodimethylaniline:



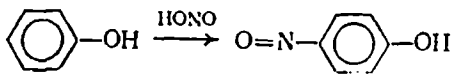
The mobility of the hydrogen atoms in the benzene nucleus is characteristic not only of aromatic amines but also of phenols (cf. Chapter 13). Phenols are therefore easy to nitrosate as well.

The nitrosating agent, electrophile, is probably the nitrosonium cation NO^+, formed from nitrous acid:

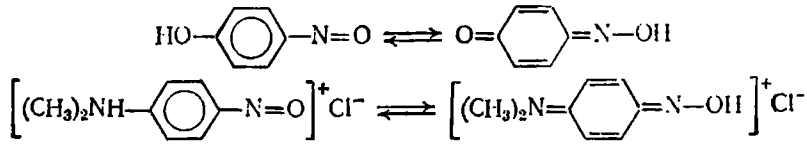
$$HONO + H^+ \rightleftharpoons H_2NO_2^+ \rightleftharpoons H_2O + NO^+$$

(see explanations to Experiments 158, 159, and 210).

Phenol reacts with nitrous acid to form *p*-nitrosophenol (m.p. 120 °C, decomposes):



Nitrosophenol (Experiment 175) and a salt of *p*-nitrosodimethylaniline are easily isomerized into the corresponding quinone oximes with the transfer of the hydrogen atom from the phenol oxygen (or amine nitrogen) to the oxygen of the nitroso group. Each of these compounds is a tautomeric mixture of the corresponding molecules:



Free *p*-nitrosodimethylaniline has no hydrogen atoms at the amine nitrogen. It does not therefore form the quinone oxime structure and, like other nitroso compounds, is green. *p*-Nitrosophenol is green only in the ether solution, whereas in the solid state it is almost colourless.

221
Reactions of Nitroso Compounds

REAGENTS

Nitrosodiphenylamine (see Experiment 218).
para-Nitrosodimethylaniline or its *salt* (see Experiment 219).
para-Nitrosophenol (see Experiment 220).
Phenol.
Diphenylamine, 0.1 per cent solution in sulphuric acid.

Carry out simultaneously tests with various nitroso compounds.

A. Place a mixture of a few crystals (0.1-0.2 g) of phenol with 0.5 volume of a nitroso compound and 3-5 drops of concentrated sulphuric acid into a test tube and heat carefully until the mixture turns dark brown or blue-green.

Cool the test tube, add 8-10 ml of water, and shake: the solution turns red or brownish red. Add, with cooling in cold water, excess (2-3 ml) of concentrated alkali solution: the specific colour develops.

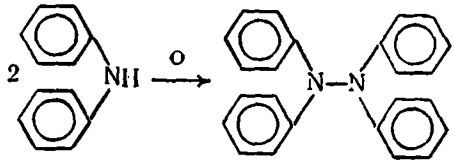
B. Place a few separate drops of a colourless solution of diphenylamine in sulphuric acid on a flat piece of glass, placed over a sheet of white paper. Using a glass rod transfer a few crystals of a nitroso compound into one such drop. The reaction manifests itself by development of intense colour.

Before transferring another test substance, thoroughly wash the glass rod and wipe it with a piece of filter paper.

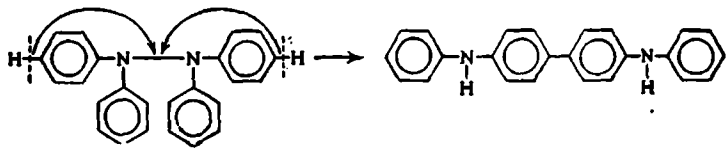
The reaction of nitroso compounds with phenol was discussed in Chapter 13 (Experiment 175). This reaction is characteristic of

both *p*-nitrosophenol and most other nitroso compounds that easily lose the nitroso group to give *p*-nitrosophenol in the presence of phenol. Since the conditions of the reaction in this experiment differ from those in Experiment 175, the shades of colour of the solutions obtained in these experiments will also differ. Blue or green colour that develops in a heated and then alkalized aqueous solution is most characteristic.

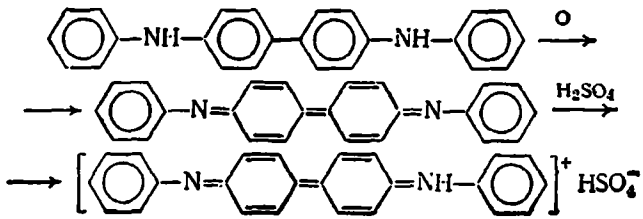
The reaction between nitroso compounds and diphenylamine is also accounted for by the easiness of elimination of the nitroso group with formation of nitrogen oxides. A solution of diphenylamine in sulphuric acid is often used to detect nitrites and nitrates. Like many other oxidants (such as hydrogen peroxide, chromates, chlorates), nitrogen oxides easily oxidize diphenylamine to convert it first into tetraphenylhydrazine



Tetraphenylhydrazine in a sulphuric acid solution undergoes the intramolecular benzidine rearrangement and converts into NN′-diphenylbenzidine (cf. Experiment 223):



In the conditions of our experiment, diphenylbenzidine is further oxidized to diphenyldiphenoquinone diimine that reacts with sulphuric acid to give an imonium salt, whose structure is also quinonoid, and which is therefore coloured intense blue:



Among the nitroso compounds dealt with in this experiment, *p*-nitrosodimethylaniline and its salt bind the nitroso group relatively faster and do not give reactions described above with phenol or diphenylamine.

222
Splitting of para-Nitrosodimethylaniline with Alkali

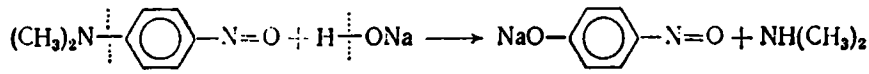
REAGENTS

para-Nitrosodimethylaniline or its *salt* (Experiment 219).
Phenol.
Diphenylamine, 0.1 per cent solution in sulphuric acid.

Mix about 0.2-0.3 g of a salt (or free base) of *p*-nitrosodimethylaniline with 2 ml of water and 1 ml of concentrated alkali solution. Boil the obtained yellow-green liquid for 2-3 minutes. The liquid first becomes clear and then gradually turns dark red. Gas is evolved in the reaction and the specific unpleasant odour of dimethylamine is felt. A red litmus paper immediately becomes blue as it is brought to the test tube mouth.

Cool the dark red solution. Add its two or three drops to a mixture of phenol and sulphuric acid and another drop to the solution of diphenylamine (see Experiment 221).

When heated in an alkaline solution, dimethylamine is eliminated from *p*-nitrosodimethylaniline to give an intensely coloured salt of *p*-nitrosophenol:



Unlike the original nitroso compound, the product of its splitting with alkali gives colour reactions (see Experiment 221 and explanations to it).

The liberated dimethylamine (b.p. 8 °C) is a much stronger base han ammonia (see Chapter 10).

223
Preparing Hydrazobenzene and Its Reactions

REAGENTS

Nitrobenzene.
Ethyl alcohol.
Zinc dust.

Place 2 ml of nitrobenzene, 12 ml of alcohol, and 3 ml of concentrated alkali solution into a 50-100 ml flask provided with a stopper and a vertical condenser tube. Stir the mixture well by shaking, heat on a boiling water bath, and gradually, within 10-15 minutes,

add 6-7 g of zinc dust. Stopper the flask after adding each next small portion. If the mixture starts vigorously boiling, cool it by dipping the flask into cold water. Then heat the flask again. The liquid first becomes orange-red, then yellow. Now add 25 ml of alcohol, heat to boiling, and transfer the liquid together with the precipitate onto a pleated filter. Add 10 ml of alcohol to the residue in the flask, heat, and transfer its contents onto the same filter.

Cool the collected filtrates in a mixture of ice and salt for an hour, then separate almost colourless crystals with suction, wash them on the filter with a cooled mixture of 1 ml of alcohol and 2 ml of water, and dry in filter paper. The yield of hydrazobenzene is 0.6-0.9 g. The product can be purified by re-crystallization from ethyl alcohol.

Hydrazobenzene does not keep, and it should therefore be immediately used in the following tests.

A. Strongly heat a greater part of the obtained product in a dry test tube. It melts, then turns bright red, and boils: a distinct odour of aniline is felt. The melt solidifies on cooling. Add 2-3 ml of alcohol, heat to dissolve the melt, and cool to 0 °C: fine red crystals of azobenzene precipitate. The alcoholic solution gives the specific reactions of aniline (see Experiments 204 and 205).

B. Shake the remaining portion of hydrazobenzene with 3 ml of water, add 1 ml of concentrated hydrochloric acid, and heat: the crystals dissolve and do not re-precipitate on cooling. Add a drop of dilute sulphuric acid: ample white precipitate of benzidine sulphate falls out. If the solution is alkalized, free benzidine precipitates.

Zinc reduces nitrobenzene in a strongly alkaline medium (cf. Experiment 202) by steps, and the colour of the reaction mixture changes accordingly. Azobenzene, which is first formed, has an intense colour which is due to the presence in its molecule of the chromophoric azo group. Azobenzene is further reduced into a colourless hydrazobenzene (m.p. 126 °C)

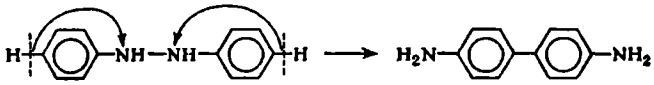
$$2C_6H_5NO_2 \xrightarrow[-4H_2O]{+8H} C_6H_5N{=}NC_6H_5 \xrightarrow{+2H} C_6H_5NH{-}NHC_6H_5$$

Hydrazobenzene was first prepared in 1845 by N. N. Zinin.

Azobenzene (m.p. 68 °C) is very stable; its phenyl groups are in the position *trans* to the double —N=N— bond. Its *cis* isomer is less stable. Hydrazobenzene quickly oxidizes in air and decomposes when heated strongly. Part of its molecules are reduced to aniline by the hydrogen atoms of other molecules of hydrazobenzene that are themselves oxidized to azobenzene:

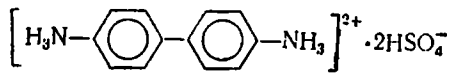
$$2C_6H_5NH{-}NHC_6H_5 \longrightarrow 2C_6H_5NH_2 + C_6H_5N{=}NC_6H_5$$

By the catalytic action of strong mineral acids, hydrazobenzene is re-arranged intramolecularly into benzidine (*p,p'*-diaminodiphenyl):



Benzidine (m.p. 128 °C) was first prepared by this method in 1845 by N. N. Zinin (in Kazan). The *benzidine re-arrangement* discovered by Zinin is now widely used in the manufacture of aniline dyes.

Being a typical amine, benzidine, unlike hydrazobenzene, reacts with acids to give salts. Its hydrochloride is readily soluble in water. For this reason, hydrazobenzene, which is converted quantitatively into benzidine in the conditions of our experiment, is fully dissolved. Benzidine sulphate



is very sparingly soluble in water and alcohol. Its solubility in water is almost the same as of barium sulphate; benzidine is therefore a sensitive reagent for the SO_4^{2-} ion and is used for its quantitative determination.

224
Formation of Aryl Hydroxylamines

REAGENTS

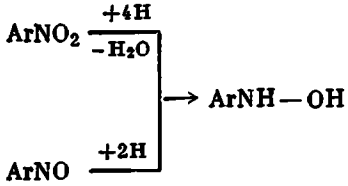
Nitrobenzene, or other aromatic mononitro- or nitroso compound.
Ethyl alcohol.
Zinc dust.
Silver nitrate, ammoniacal solution (Experiment 60).
Benzoyl chloride.

Dissolve a few drops of nitrobenzene in 2 ml of alcohol, add 1-2 ml of water, 2-3 drops of concentrated acetic acid, and heat the mixture to boiling. Add, in small portions, 0.2-0.3 g of zinc dust, slightly heat the foaming mixture again, and allow to stand for 5-7 minutes. Pass the mixture through a small filter wetted with water.

A. Add a small quantity of ammoniacal silver nitrate (cf. Experiment 60) to part of the filtrate (its cloudiness is allowed).

B. Add 1-2 drops of benzoyl chloride to the other part of the filtrate, heat to boiling, cool, acidify with a drop of concentrated hydrochloric acid, and add, in small portions, ferric chloride solution until the mixture develops colour.

The reduction of aromatic mononitro- or nitroso compounds in a neutral or weakly acid medium gives a mixture of products in which aryl hydroxylamines predominate:



These are very weak bases and energetic reductants. They react with acid chlorides to give substituted hydroxamic acids, which are characterized by the bright colour of their iron salts (cf. Experiments 111, 113, and 195).

Azoxy- and azo compounds are reduced in these conditions to hydrazo compounds or substituted hydrazines. These substances also rapidly liberate silver from its ammoniacal solution, but do not form hydroxamic acids.

The reduction of nitro compounds in alkaline or strongly acid medium has been discussed above (see Experiments 202 and 223).

QUINONES. PHTHALEINS. TRIPHENYLMETHANE DERIVATIVES

Quinone, anthraquinone, alizarin, phenolphthalein, fluorescein, eosin, fuchsin, methyl violet, and triphenylcarbinol will be used in the experiments of this chapter. Quinone of good purity is prepared in Experiment 225; triphenylcarbinol can also be prepared by the students (Experiment 257). It is desirable that the other substances be kept ready for use in the laboratory.

Melting points of some of these substances are given in Table 14.

Fluorescein, eosin, fuchsin, and methyl violet are decomposed on heating and in normal conditions have no sharp melting points.

225
Preparing para-Quinone and Its Reactions

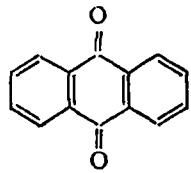
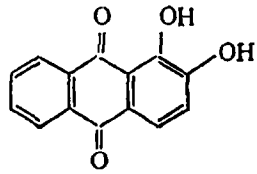
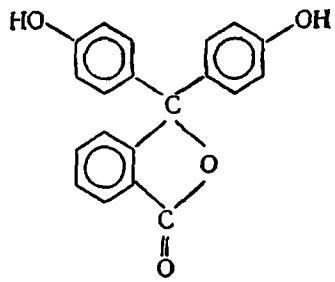
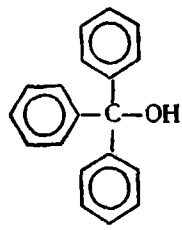
REAGENTS

Hydroquinone.
Potassium dichromate, powder.
Sodium sulphite.

Place 1 g of hydroquinone, 3 g of potassium dichromate, and 20 ml of water into a small flask provided with an outlet tube and a wide tube condenser. The mixture darkens gradually and strongly thickens (quinhydrone crystals precipitate). Add 1 ml of concentrated sulphuric acid, drop a boiling stone, and heat the mixture over a burner until it boils energetically. Collect the distillate in a test tube. Yellow vapour of quinone is first evolved, then a few millilitres of its aqueous solution are distilled rapidly, and bright yellow crystals are accumulated in the condenser tube. Discontinue the distillation when the quantity of the crystals stops growing. Dismantle the apparatus, push out

Table 14

Melting Points of Quinones, Phenolphthalein, and Triphenylcarbinol

Substance	Formula	Melting point °C
para-Quinone		116
Anthraquinone		286
Alizarin		289
Phenolphthalein		254
Triphenylcarbinol		163

the crystals from the tube (using a wire or a glass rod), and dry them by suction and in filter paper. Note the specific odour of quinone.

The yield is 0.6-0.8 g.

Use the aqueous solution in the following tests.

A. Dissolve a few crystals of sodium sulphite in 1 ml of water and acidify the solution with dilute sulphuric acid until a clear odour of sulphurous anhydride is felt. Slowly add part of this liquid, drop by drop, to 2-3 ml of a saturated quinone solution, with shaking, until the precipitate that first falls out is all dissolved.

B. Add a small amount of quinone solution to the clear solution obtained in test A and note the changes.

C. Add a small amount of potassium iodide solution to 1-2 ml of quinone solution, and then put 1-2 drops of dilute sulphuric acid.

D. To 1-2 ml of quinone solution add an equal volume of dilute alkali. The liquid immediately turns brown. Acidify the mixture in a few minutes: brown flakes precipitate.

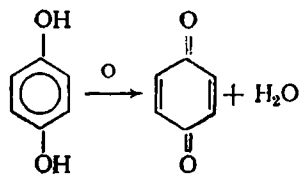
226
Preparing Quinhydrone

REAGENTS

Quinone (see Experiment 225).
Hydroquinone.
Ethyl alcohol.

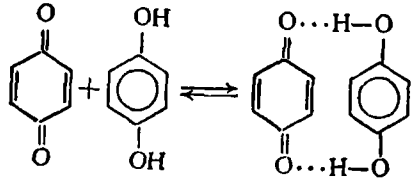
Place 0.5 g of hydroquinone into a small beaker, add 30 ml of water, and gently heat to dissolve the crystals. Dissolve 0.5 g of quinone in another test tube in 8-9 ml of alcohol. Add this solution to the warm hydroquinone solution. Place the beaker in cold water for 10-15 minutes: greenish-black crystals of quinhydrone precipitate. Separate them on a filter with suction, wash with a small quantity of cold water, and dry in filter paper. The yield is almost theoretical.

Dichromates in an acid medium are strong oxidants (see explanations to Experiment 48). Hydroquinone is oxidized in our experiment to give *p*-benzoquinone:



The exact formula of quinone was established in 1837 by A. A. Voskresensky, who was the first to isolate this substance.

First, when the reaction mixture contains an excess of the original hydroquinone, quinone reacts with it to give quinhydrone that easily falls into its constituents:



Quinhydrone can also be prepared by directly mixing quinone and hydroquinone. The molecules of the starting substances are bound in quinhydrone not only by the hydrogen bonds but also by the transfer of part of the charge of the π-electrons of the benzene nucleus from hydroquinone to quinone (see explanations to Experiment 163).

Quinhydrone has an intense colour, is almost odourless, and sparingly soluble in water. It is often used in potentiometric determination of hydrogen ion concentration, i.e. of acidity of solutions (quinhydrone electrode). The melting point of quinhydrone is 171 °C, i.e. the substance melts at a temperature higher than the melting point of each of its separate components (cf. Experiment 8).

By further oxidation the entire hydroquinone (i.e. both free and bound in quinhydrone) is passed into benzoquinone. The latter substance has an irritating odour and is very volatile despite the relatively high melting point. It should therefore be kept in tightly stoppered bottles. The bright colour of quinone illustrates the effect of the quinoid group of atoms on the colour of a compound.

In the described conditions for preparing quinone, potassium dichromate can be replaced by a more soluble salt $Na_2Cr_2O_7$ and also by manganese dioxide.

Quinone readily takes part in various reactions, mainly addition reactions (at double bonds C=C or C=O). Reduction of quinone by sulphur dioxide, hydrogen disulphide, nascent hydrogen, etc. gives hydroquinone that reacts at the beginning of the reaction with excess quinone to precipitate quinhydrone. By further reduction, quinhydrone is all dissolved to pass into hydroquinone. Being a strong oxidant, quinone rapidly liberates iodine from potassium iodide in an acid medium. This reaction is used for quantitative determination of quinone.

High-molecular amorphous acid products are produced from quinone in an alkaline solution. Their properties are very similar to those of humic acids of soil.

Benzoquinone is the simplest quinone. More complicate substances of this type (e.g. some vitamins, pigments, and antibiotics) are of vital importance for many organisms.

227
Formation of Anthraquinone from Anthracene

REAGENTS

Anthracene.
Chromic anhydride or *sodium dichromate*, 20 per cent solution.
Zinc or *aluminium*, powder.

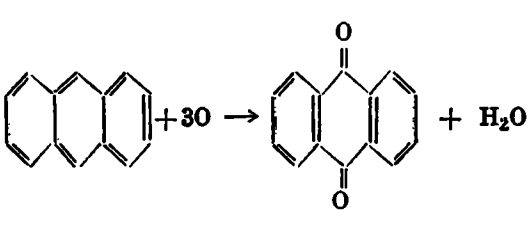
Place 0.1-0.2 g of anthracene and 2 ml of glacial acetic acid in a test tube and heat to boiling to dissolve the greater part of anthracene. Cool the mixture, add 2 ml of concentrated sulphuric acid, and then, drop by drop, 1 ml of chromic anhydride or sodium dichromate. The mixture becomes hot. Boil the green mixture for a few minutes, then cool, and pour into 10-15 ml of water.

Yellowish flakes precipitate from the green aqueous solution. Separate them on a small paper filter and wash with hot water until the filter becomes colourless. Wash the precipitate down into the filter cone, allow the water to drip off, remove the moist filter from the funnel, tear off the cone tip containing the precipitate, and place it into a test tube. Add 2-3 ml of dilute alkali solution and a small portion of zinc or aluminium powder, and heat the mixture to boiling.

Simultaneously heat a mixture of zinc (aluminium), alkali and the sample of the starting anthracene.

When hydrogen liberation discontinues, the liquid turns bright red, but as it is shaken, the colouration disappears. This indicates the presence of antraquinone (see Experiment 228).

Anthracene (m.p. 217 °C) is readily oxidized to anthraquinone:



by the action of various oxidants, e.g. chromic acid, potassium permanganate, etc. Even nitric acid acts on anthracene mainly as an oxidant, and not as the nitrating agent.

The further oxidation of anthraquinone is difficult to realize. Anthraquinone is insoluble in water.

228
Reduction of Anthraquinone

REAGENTS

Anthraquinone.
Zinc or *aluminium*, powder.

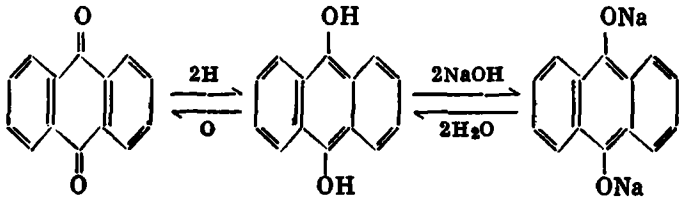
Place a few crystals of anthraquinone and 2-3 ml of dilute alkali solution into a test tube and heat the mixture to boiling. There are no visible changes. Add a small quantity of aluminium or zinc powder and continue heating for 1-2 minutes. Cool the mixture. When hydrogen bubbling stops the liquid turns bright red. Shake the solution: the colour vanishes. Heat the mixture with a new portion of the powder. The red colour develops again and vanishes on shaking.

Aluminium and zinc are dissolved in alkali solutions to liberate hydrogen:

$$Al + OH^- + 3H_2O \longrightarrow [Al(OH)_4]^- + 3H$$

$$Zn + OH^- + 2H_2O \longrightarrow [Zn(OH)_3]^- + 2H$$

Hydrogen reduces anthraquinone to anthrahydroquinone, whose disodium salt is readily dissolved in water to give coloured solution in which it is appreciably hydrolysed:



As the mixture is shaken, air oxygen oxidizes anthrahydroquinone to anthraquinone, and the liquid is decolourized.

229
Alizarin Reactions

REAGENTS

Alizarin.
Aluminium-potassium sulphate (alum), saturated solution.
A *piece of yarn* or a *white washed fabric* is required for test C.

Place 0.1 g of alizarin and 8-10 ml of water in a test tube and shake. Add 1-2 ml of dilute alkali solution to the obtained suspension: a deep violet-blue colour develops. Use the solution in the following tests.

A. Acidify 1-2 ml of the alkaline alizarin solution with hydrochloric acid: the solution is decolourized and free alizarin precipitated.

B. Add a few drops of the alum solution to 1 ml of the alkaline alizarin solution: orange-red flakes of aluminium-alizarin 'lake' are formed.

C. Impregnate a piece of a white fabric or yarn in the alum solution. Press out excess liquid, immerse the material into the alkaline alizarin solution heated almost to boiling, and keep for 3-4 minutes, stirring with a glass rod at short intervals. Remove the material and rinse in warm water. The material is dyed red. The dye does not run into water.

Alizarin (1,2-dihydroxyanthraquinone) is insoluble while its disubstituted phenolates with alkali metals readily dissolve in water. Alizarin forms coloured salt-like complex compounds with metal ions. Such compounds containing aluminium, chromium, or iron, known as alizarin lakes, are insoluble in water nor do they hydrolyse in it. Formed on the surfaces of fibre or fabric, that are preliminarily treated with surfactants and then with a solution of a salt of any of these metals (a mordant), the lakes are fastly affixed to the dyed material. Mordant dyeing is now widely used in industry.

230
Formation of Phthaleins

REAGENTS

Phthalic anhydride or *o-phthalic acid.*
Phenol.
Resorcinol.
alpha- and *beta-Naphthols.*

Carry out simultaneously tests with various phenols.

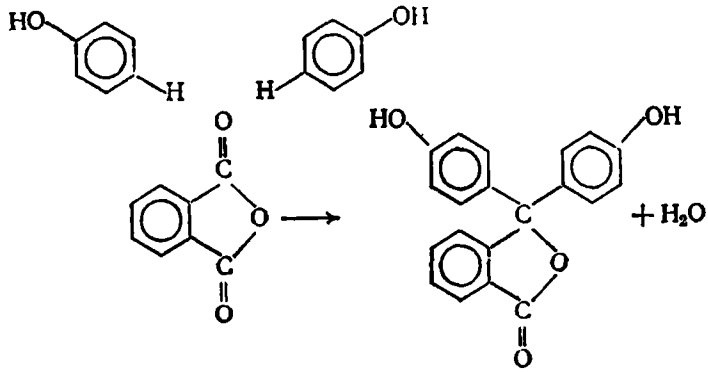
Place 0.05-0.1 g of powdered phthalic anhydride (phthalic acid) in a dry test tube and add about two weights of the phenol in question. Shake the test tube to mix the components, add 1-2 drops of concentrated sulphuric acid, and carefully heat over a burner. Discontinue the heating when the melt starts bubbling.

Allow the test tube to cool, add 5-7 ml of water, and shake. Transfer part of the obtained acid solution into another test tube and add first alkali solution, drop by drop, until the colour changes, and then dilute acid to restore the original colour (or until the solution is decolourized).

Phthalic anhydride is easily formed by heating *o*-phthalic acid (Experiment 190). It can be condensed with many phenols (with

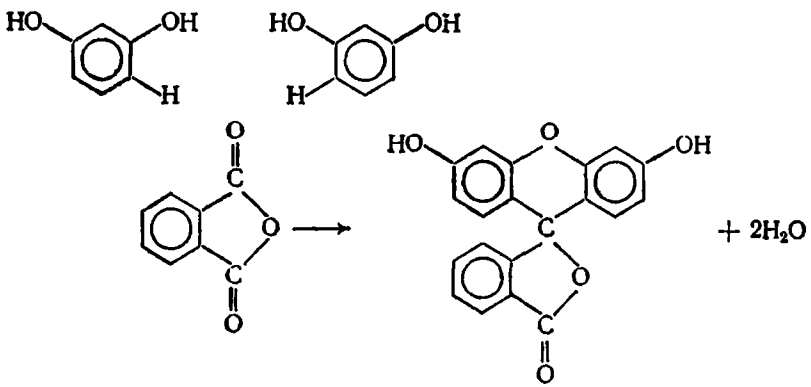
non-substituted hydrogen atom in the para position) to give triphenylmethane derivatives. The condensation reaction is accompanied by the elimination of a water molecule formed by the oxygen of one of the carbonyl group of the anhydride and mobile hydrogen atoms of the benzene nuclei of two phenol molecules. The condensation is much facilitated by the introduction of dehydrating agents, such as concentrated sulphuric acid or zinc chloride.

Phenol, C_6H_5OH, gives mostly phenolphthalein in the described conditions:



Phenolphthalein is used in medicine as a laxative.

Dihydric phenols with the hydroxyl groups in the meta position can also enter into the condensation reaction to eliminate another molecule of water on account of the hydroxyl groups of two phenol molecules with formation of a six-membered ring. For example, resorcinol gives resorcinolphthalein (fluorescein):



Some phthaleins are colourless in neutral and acid solutions (phenolphthalein). Others are coloured (fluorescein). Colourless phthaleins give characteristic red, green, or blue colour in alkali solution, which is explained by the formation of salts having the quinonoid structure (see Experiment 231).

Fluorescein produces a green fluorescing colour in an alkaline solution whose intensity is so high that it can easily be detected with negligibly small concentrations (1 : 40,000,000). This phenomenon is used to reveal the ways of water filtration in soil or in hydrotechnical construction.

Naphthols are also condensed with phthalic anhydride: alpha-Naphtholphthalein is blue-violet in an alkaline solution, and beta-naphtholphthalein produces blue-green fluorescence.

Some phthaleins are used in dyeing.

231
Alkaline Salts of Phenolphthalein

REAGENTS

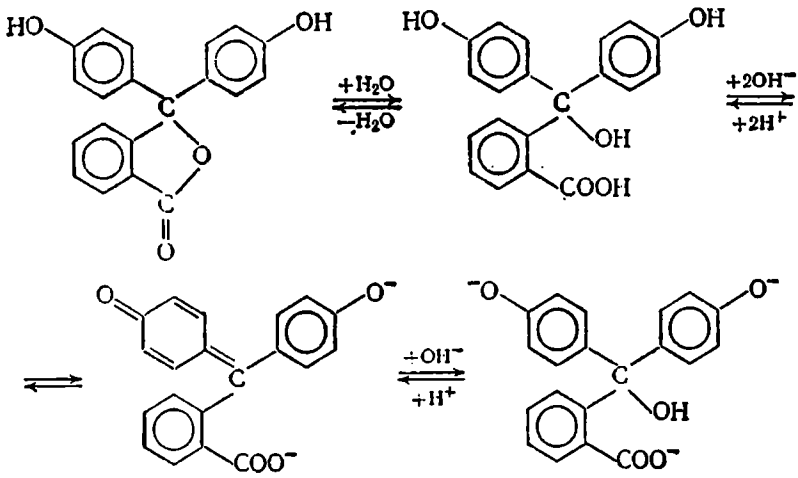
Phenolphthalein, 1 per cent solution in alcohol.

Place 2-3 ml of water in a test tube and add two drops of alcoholic solution of phenolphthalein: the mixture becomes slightly cloudy. Add a drop of dilute alkali solution: the cloudiness disappears and the liquid turns crimson. Add 0.5-1 ml of alkali in excess: the mixture is gradually decolourized again.

Add sulphuric acid, drop by drop, to the colourless strongly alkaline solution. The liquid turns crimson but then is decolourized again.

The lactone ring of phenolphthalein molecule in an alkaline solution is easily hydrolysed; the formed *p*,*p*′-dihydroxytriphenylcarbinol-*o*-carboxylic acid gives a salt. The atoms of the carboxyl hydrogen and of one phenol hydroxyl are ionized, and a molecule of water is eliminated between the other phenol hydroxyl and the alcohol hydroxyl. The double-charge anion formed in this solution has the quinonoid structure and gives the crimson colour to the solution. In the presence of excess alkali, the second phenol hydroxyl is ionized and neutralized as well to rule out the formation of the quinonoid structure. The triple-charge anion of the trisubstituted salt of phenolphthalein is therefore colourless.

Gradual acidification reverses the reaction sequence:



232
Bromination of Fluorescein

REAGENTS

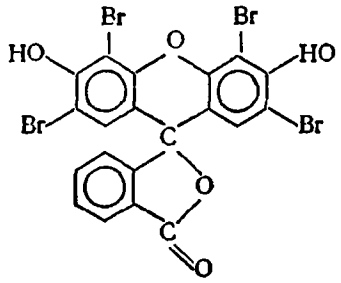
Fluorescein, pure, or in solution (see Experiment 230).
Bromine water, saturated solution.
Ethyl alcohol.

Dissolve a few grains of fluorescein in 2-3 ml of alcohol with slightly heating the mixture. Divide the yellow (almost non-fluorescing) solution into two approximately equal portions. Add 4-5 ml of water to one and 2-3 ml of bromine water to the other portion. The solutions become cloudy. Add dilute alkali solution to both mixtures, drop by drop, until the colour stops changing. A bright green fluorescing solution is obtained in one test tube and a red solution of eosin in the other.

If the solution of fluorescein obtained in Experiment 230 is used, no alcohol is added.

Fluorescein is sparingly soluble in water. If its alcoholic solution is diluted with water, fluorescein is formed as yellow cloudiness.

Like in the case with phenols (see Experiment 167), fluorescein is easy to brominate. The resultant product is tetrabromofluorescein (eosin):



Eosin is even less soluble in water and precipitates in the form of an orange substance. Alkali reacts with eosin to give a readily soluble bright-red monosodium salt. The lactone ring is opened (which is common for phthaleins), and the quinonoid structure is formed.

Eosin salts are often used in the manufacture of red ink.

233
Reduction of Phthaleins

REAGENTS

Phenolphthalein, solution.
Fluorescein, solution.
Eosin, solution.
Zinc or *aluminium*, powder.

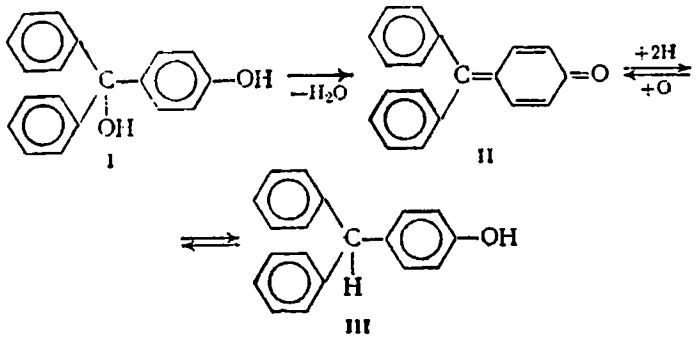
Prepare phthalein solutions by shaking a few grains of each substance with 1 ml of water, or use the solutions prepared in Experiments 230 and 232.

Place 2-3 ml of dilute alkali solution into a test tube and add a solution of phthalein in question. Now add a small portion of zinc or aluminium powder and shake without heating: much hydrogen is evolved and the liquid is decolourised.

Transfer part of the colourless liquid onto a watch glass or a porcelain dish. On exposure to air, the liquid colour is restored. Transfer the remaining liquid into a test tube and add dilute sulphuric acid drop by drop. The original colour is restored faster than in the previous case.

The colour of alkaline solutions of phthaleins is due to the presence in them of molecules with quinonoid structure(II) that are formed

by elimination of water from the substituted triphenylcarbinol(I) (see Experiment 231). For example:



Zinc (aluminium) reacts with alkali to liberate hydrogen (Experiment 228), which reduces the quinonoid compound to a colourless benzoid compound (III) (leuco base), whose hydroxyl groups react with excess alkali to give phenolate. Atmospheric oxygen gradually oxidizes the leuco compound to the original coloured substance. Acidification binds part of alkali to liberate the leuco base from the phenolate and to facilitate its oxidation.

234
Reactions of Fuchsin and Methyl Violet with Acids and Alkalis

REAGENTS

Parafuchsin.
Methyl violet.

Carry out simultaneously tests with fuchsin and methyl violet.

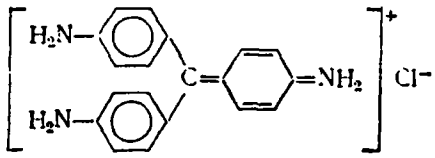
Prepare intensely coloured solutions of the reagents by dissolving their few crystals in 3-5 ml of water. Divide each solution into two parts.

Add dropwise concentrated hydrochloric acid to one of these parts: the colour changes to brown or yellow. Strongly dilute the acid solution with water: the original colour is gradually restored.

Take the other part of the starting solution and add dilute alkali, drop by drop. The liquid is gradually decolourized and flakes of free base precipitate. Carefully acidify the mixture: the precipitate is dissolved and the original colour restored. If excess acid is added, the colour changes to brownish yellow.

Parafuchsin differs from its higher homologue fuchsin (see Experiment 61) only by the absence of the methyl group at one of the

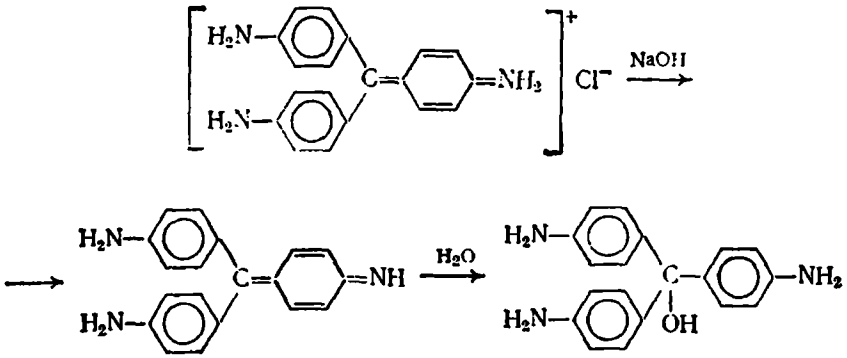
benzene rings. It is a basic dye of the triphenylmethane series and is actually a salt formed with one equivalent weight of acid:



In the aqueous solution the salt is almost completely ionized and the bright colour is due to the presence of a univalent cation having the quinonoid structure.

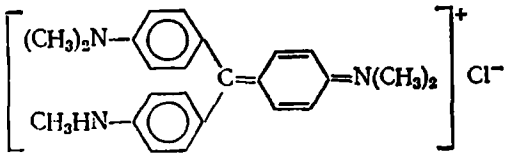
In the presence of excess acid, amine salts are formed with two or even three equivalent weights of the acid (at the expense of the second and the third amino group). These salts give a brown-yellow solution, and in a great excess of acid the solution becomes almost colourless because the ionization degree decreases. When the solution is diluted with water, the salts are easily hydrolysed to liberate the acid and the intensely coloured original salt formed with one equivalent weight of the acid.

In the presence of excess alkali, a very unstable free base is formed from the amine salt. The base rapidly combines with water to give sparingly soluble triaminotriphenylcarbinol:



This carbinol base (pseudobase) has no quinonoid group and is not a dye. Alkali therefore decolourizes the solution of the original substance. The acidification reverses the sequence of the conversions.

Methyl violet differs from parafuchsin in that it has five methyl groups at the nitrogen atoms:



The conversions of this dye on acidification and alkalization of its solutions are absolutely the same as those observed with parafuchsin. The only difference is that an intermediate green colour of the salt formed with two equivalent weights of acid can be observed in the transition of the violet colour to yellow-brown as the solution is acidified (and reverse).

235
Formation of Aurine

REAGENTS

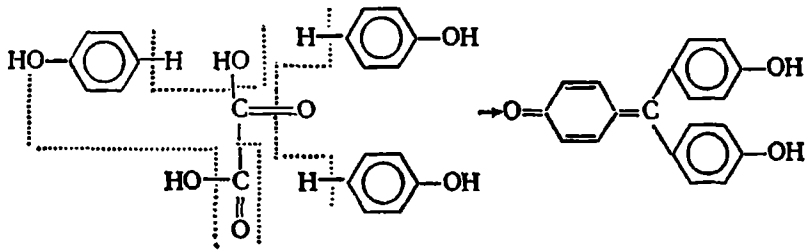
Phenol.

Oxalic acid, powder, or *carbon tetrachloride* and solid *sodium hydroxide.*

Place about 0.02-0.05 g of oxalic acid into a dry test tube and about double quantity of crystalline phenol. Shake the test tube slightly to mix the substances, wet the mixture with 1-2 drops of concentrated sulphuric acid, and heat carefully over a burner until the mixture starts boiling and an intense yellow colouration develops. (If carbon tetrachloride is used, add its few drops to about an equal quantity of phenol, drop a grain of solid sodium hydroxide, and heat slowly over a burner until the mixture solidifies.)

Cool the test tube, add 3-4 ml of water to the solid product, and shake: a bright coloured solution is formed. Acidification or alkalization changes the colour.

As the mixture is heated in the presence of sulphuric acid one molecule of oxalic acid is condensed with three molecules of phenol to eliminate water and carbon monoxide with formation of aurine:



In the reaction with carbon tetrachloride, its carbon atom becomes the central carbon atom in the aurine molecule.

The comparison of structural formulas of aurine, phenolphthalein (Experiment 230), and parafuchsin (Experiment 234) shows close affinity between these coloured compounds: they all are derivatives of triphenylmethane whose one aromatic ring has the quinonoid structure.

Aurine is an acid triphenylmethane dye, and, just like other substances of this type, its colour depends on the acidity of the medium. Aurine is often used as an indicator in acidimetric titration.

The yellow colour of the solution is explained by non-dissociated molecules of aurine and the red colour, by its ions.

236
Formation of Carbonium Salts of Triphenylmethyl

REAGENTS

Triphenylcarbinol (see Experiment 257).

Dissolve 0.02-0.05 g of dry triphenylcarbinol in 2-3 ml of glacial acetic acid with slightly heating the mixture. Divide the cooled almost colourless solution into two parts. Add a few drops of concentrated sulphuric acid to one and about the same quantity of concentrated hydrochloric acid to the other portion. Bright coloured clear solutions are formed.

Add water in small portions to both solutions. The colour completely vanishes and the original carbinol is produced in the form of a white cloudiness.

Triphenylcarbinol and some other triphenylmethane derivatives react with strong concentrated acids to give coloured salt-like complex compounds containing the positive ion of triphenylmethyl:

$$(C_6H_5)_3C-OH+H_2SO_4 \rightleftharpoons H_2O+[(C_6H_5)_3C]^+HSO_4^-$$

The phenomenon is known as 'halochromia' (Gr. *halōs* salt + *chroma* colour; hence colouring by salt), and the salts containing such ions with the central carbon atom are given the name of *carbonium salts* (by analogy with ammonium and oxonium salts; the analogy is only apparent since the central atom here does not bind hydrogen atom).

Excess water easily hydrolyses the carbonium salt to shift the equilibrium to the left (see also explanations to Experiment 27).

237
Formation of Free Triphenylmethyl

REAGENTS

Triphenylcarbinol (see Experiment 257).
Hydrogen chloride, dry gas.
Benzene.
Zinc dust.
Iodine, very dilute brownish solution in alcohol.

To prepare hydrogen chloride, place 2-3 g of sodium chloride and 2-3 ml of concentrated sulphuric acid into a test tube, stopper with a plug through which an outlet tube is passed, and heat slightly. Pass the liberated gas through a tube packed with granulated calcium chloride.

Place 0.3 g of dry triphenylcarbinol in a dry test tube provided with an outlet tube (Fig. 1) and dissolve it in 5 ml of benzene. Pass a jet of hydrogen chloride into the solution through a tube with a drawn end. Perform this operation in the HOOD. The clear solution becomes cloudy and can turn slightly yellow. Stop passing the gas in 5-6 minutes, add a boiling stone, close the test tube with a stopper, and connect a tube condenser. Heat the liquid over a burner to distil about half volume of benzene. The formed water and excess hydrogen chloride are also distilled.

Transfer the colourless or slightly yellowish bottoms into a small dry test tube (the liquid must fill at least 3/4 volume of the test tube). Add about 1 g of zinc dust, close the test tube tightly with a rubber plug, and shake strongly. The solution over the precipitated zinc turns bright orange.

Decant part of the coloured liquid into a separate test tube and shake (to ensure a better contact with the air) or blow air through the liquid using a rubber bulb. The clear liquid turns cloudy, and its colour almost vanishes. The colour can be restored on standing, but as the solution is brought into contact with air, the colour can vanish again.

Add, drop by drop, alcoholic solution of iodine to the other part of the orange solution of triphenylmethyl. As the coloured liquids are mixed together, the resultant solution is decolourized.

Hydrogen chloride easily converts the tertiary alcohol triphenylcarbinol into triphenylchloromethane (cf. explanations to Experiment 96):

$$(C_6H_5)_3C-OH + HCl \longrightarrow H_2O + (C_6H_5)_3CCl$$

It remains dissolved in benzene.

When acted upon with zinc (cf. Experiment 34), it gives a colourless hydrocarbon hexaphenylethane. About 5-10 per cent of hexaphenylethane molecules decompose in solution to give the free radical triphenylmethyl:

$$(C_6H_5)_3C\text{—}C(C_6H_5)_3 \rightleftharpoons 2(C_6H_5)_3C\cdot$$

The presence of triphenylmethyl can be detected by the bright yellow colour of its solution (cf. Experiment 236), but unlike in the previous experiment, triphenylmethyl here is electrically neutral. Triphenylmethyl is highly reactive. It rapidly reacts with halogens and many other substances. It also reacts with atmospheric oxygen to give a colourless peroxide sparingly soluble in benzene:

$$2(C_6H_5)_3C\cdot + O_2 \longrightarrow (C_6H_5)_3C\text{—}O\text{—}O\text{—}C(C_6H_5)_3$$

The yellow colour vanishes but it can re-appear because of the shift of the equilibrium of the reversible reaction to the right and dissociation of the remaining non-dissociated hexaphenylethane molecules.

Triphenylmethyl binds free iodine to give triphenyliodomethane.

Triphenylmethyl was the first investigated organic compound containing tervalent carbon (M. Gomberg, 1900). Many other similar compounds, known as *stable carbon free radicals*, were discovered and studied later. Some of them were prepared not only in solution form but also as individual substances. A. E. Chichibabin and A. E. Arbuzov made an important contribution to the study of this section of organic chemistry. It has been established recently that the dimer of triphenylmethyl is not a true hexaphenylethane, and one of its six-membered nuclei has the structure of cyclohexadiene.

HETEROCYCLIC COMPOUNDS

Pyridine, quinoline, and indigo should be kept ready for use in the experiments with heterocyclic compounds given in this chapter. Uric acid and nicotine can be prepared in the laboratory from natural material. Furfural solution can be prepared during the experiment (Experiment 238).

To prepare uric acid, place 40-50 ml of fresh urine in a porcelain dish, add 2-3 ml of concentrated hydrochloric acid, and allow to stand for a few hours. Carefully decant the reddish liquid. Crystals of uric acid remain on the bottom. They are coloured by impurities and look like sand. Wash them with a few drops of water in the same dish and use in Experiment 247.

To prepare nicotine solution, thoroughly grind 10-15 g of tobacco in a mortar with 3-5 g of hydrated lime and a small quantity of water, and transfer the mass into a distillation flask. Add 70-100 ml of water, drop a few boiling stones, connect a condenser, and distil 30-40 ml of liquid. The clear, or slightly cloudy, distillate smells of nicotine and gives the specific reactions.

Some constants of heterocyclic compounds are given in Table 15.

238
Formation of Furfural from Pentosans

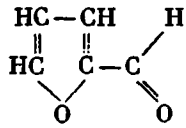
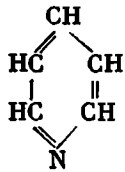
REAGENTS

Any plant material rich in pentosans, e.g. *brans, cherry gum, wood saw-dust, peanut hulls, crushed corn cobs, shells of sunflower seeds.*

Place about 1 g of crushed pentosan-containing material into a test tube and mix by shaking with 2-3 ml of concentrated hydrochloric acid, 4-5 ml of water, and a few drops of ferric chloride solution. Heat the mixture for 15 minutes on a boiling water bath,

Table 15

Properties of Heterocyclic Compounds

Substance	Formula	M. p., °C	B. p., °C	Density, g/cc
Furfural		−37	162	1.16
Pyridine		−42	115	0.98
Quinoline		Below −15	238	1.1
Indigo	$C_{16}H_{10}O_2N_2$	390-392	Sublimes	—
Uric acid	$C_5H_4O_3N_4$	Decomposes	—	1.89
Nicotine	$C_{10}H_{14}N_2$	Below −10	247	1.01

then connect an outlet tube (Experiment 6) and heat the test tube carefully over a burner to distil 1-2 ml of liquid into another test tube. The distillate smells of furfural and gives characteristic reactions.

239
Reactions of Furfural

REAGENTS

Furfural.
Ammoniacal silver oxide solution.
Schiff's reagent.
Phenylhydrazine hydrochloride.
Sodium acetate.
Aniline.
Phloroglucinol.

Dissolve 0.5-0.6 g of furfural in 10 ml of water with shaking. If the furfural was kept for a long time and got dark, clarify it by distillation. Aqueous solution of furfural prepared in Experiment 238 can be used in tests A, B, D, and E.

Pass the aqueous solution of furfural through the following tests.

A. Carry out the reaction with Schiff's reagent (see Experiment 61).

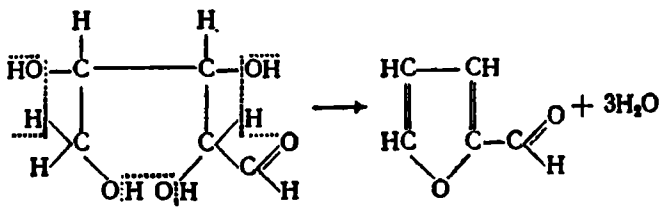
B. Carry out the reaction with ammoniacal silver oxide (see Experiment 60).

C. Carry out the reaction with phenylhydrazine (see Experiment 179).

D. Place equal volumes (a few drops) of aniline and glacial acetic acid into a small test tube or on a watch glass and mix. Wet a piece of filter paper in this mixture, press out excess liquid, and place a drop of furfural solution on the wet paper: a bright pink-red spot develops. The paper also gets coloured if kept in the vapour of a boiling mixture of the starting material with hydrochloric acid.

E. Add 3-5 drops of hydrochloric acid to 1-2 ml of furfural solution. Drop a few crystals of phloroglucinol and heat the mixture: the solution turns dark green. Dilute the solution with water: a dark precipitate falls out.

Many plants and gums of vegetable origin contain pentosans having the type formula $(C_5H_8O_4)_n$. When heated with acids, pentosans are hydrolysed to give pentoses $C_5H_{10}O_5$, mostly stereoisomeric aldopentoses, xylose and arabinose. Pentoses react with hot hydrochloric acid to eliminate three molecules of water and to give the heterocyclic aldehyde, furfural:



Ferric chloride catalyses the reaction.

Unlike hydroxymethylfurfural, which is formed in the same conditions from hexoses (see Experiment 128), furfural is stable in acid and volatile in steam. Therefore, the colour reaction with aniline in the distillate or vapour of the boiling liquid, reveals the formation of furfural, and hence the presence of pentoses or pentosans in the starting material.

The colour reaction of furfural with aniline is due to the formation of condensation product: the furane ring is opened to give saturated oxyamine, $C_6H_5NH—CH=CH—CH=C(OH)—CH=NC_6H_5$, that reacts with the acid to give salt. The presence of conjugated double bonds accounts for the bright colour of the product.

Furfural rapidly reduces silver salts in the cold, but produces only weak colouration with Schiff's reagent. Phenylhydrazone of furfural is obtained in the form of oil that quickly crystallizes. The melting point is 97 °C.

The equation of the reaction in which furfural is condensed with phloroglucinol is as follows:

$$C_5H_4O_2 + C_6H_3(OH)_3 \longrightarrow C_{11}H_8O_3 + 2H_2O$$

The coloured condensation product is very sparingly soluble in water. This is used in a gravimetric method for determining furfural and the substances that can give it, viz., pentosans or gums.

The method for preparing furfural from brans was developed in Russia by A. N. Engelgardt in 1870.

240
Formation of Pyrrole and Furan

REAGENTS

Mucic acid (see Experiment 136).
Pine splints.

Use the HOOD.

A. Place 0.1-0.3 g of mucic acid into a test tube, add 0.5 ml of concentrated ammonia solution, and carefully heat the mixture with shaking almost to dryness. Cool the test tube, add 0.5-1 ml of aqueous ammonia, and evaporate to dryness. Continue heating the dry residue until it begins bubbling, and put a pine splint wetted with a drop of concentrated hydrochloric acid into the test tube. The rising vapour of pyrrole colours the splint bright red.

B. Place 0.3-0.5 g of mucic acid into a dry test tube and heat until it begins decomposing. Continue the heating and put a splint wetted with a drop of concentrated hydrochloric acid into the upper part of the test tube. The splint is coloured green by the evolving furan. The colour gradually fades.

In Test A, mucic acid first gives an ammonium salt:

$$HOOC(CHOH)_4COOH \xrightarrow{2NH_4OH} NH_4OOC(CHOH)_4COONH_4$$

When heated, the ammonium salt falls into a complicate mixture of products, one of which is pyrrole:

$$NH_4OOC(CHOH)_4COONH_4 \longrightarrow \begin{matrix} CH=CH \\ | \quad\quad \rangle NH \\ CH=CH \end{matrix} + 2CO_2 + NH_3 + 4H_2O$$

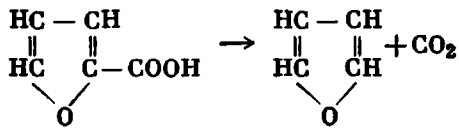
This reaction resembles the formation of derivatives of furan (oxygen analogue of pyrrole) from carbohydrates (see Chapter 11 and Experiment 238).

If succinic acid is used instead of mucic acid, add a small quantity of zinc or aluminium dust to the mixture of the acid and ammonia solution, evaporate the mixture to dryness in a dish, and heat the dry residue in a test tube.

Pyrrole (b.p. 130 °C) has a specific odour. It is more stable in an alkaline or neutral medium. Acids easily resinify it and colour it red. Other substances containing the pyrrole ring, for instance indole, also produce the specific colour on a pine splint wetted with hydrochloric acid.

Pyrrole derivatives (chlorophyll, hemin, many co-enzymes) are of vital importance in many biological processes.

When heated, free mucic acid (Test B) first loses three moles of water and a mole of CO_2. The five-membered heterocycle is closed to form furoic acid (alpha-furan carboxylic acid). It melts at 133 °C and boils at 230 °C. When its vapour is heated to temperatures over 275 °C, the acid is decarboxylated into volatile furan (b.p. 32 °C):



The structure of 'pyrrolic red' and of the green product that are formed by the action of pyrrole and furan on the splint respectively has not been established.

241
Reactions of Pyridine

REAGENTS

Pyridine.
Picric acid, saturated solution.
Tannic acid, 10 per cent solution.
Mercuric chloride, 3-5 per cent solution.

Mix 1 ml of pyridine with 5 ml of water to prepare a solution that will be used in the tests that follow below. Note the specific odour of pyridine.

A. Place a drop of pyridine solution on a red litmus paper. Add 0.5 ml of the same solution to 1 ml of ferric chloride solution: ferric hydroxide precipitates.

B. Mix equal volumes (0.5-1 ml) of pyridine, potassium permanganate, and soda solutions. The colour of potassium permanganate

persists at room temperature; neither does it vanish with heating to boiling.

C. Add 0.3-0.5 ml of pyridine to 2-3 ml of picric acid solution. Allow the mixture to stand for 5-10 minutes. Pyridine picrate gradually precipitates as beautiful needles. Add 1-1.5 ml of pyridine in excess: the crystals dissolve.

D. Mix 2-3 ml of tannic acid with 0.5-1 ml of pyridine solution. White substance precipitates at once.

E. To 0.5-1ml of pyridine solution add an equal volume of mercuric chloride solution (POISON!). A bulky white substance precipitates. Add, with shaking, first 2-3 ml of water and then 0.5 ml of concentrated hydrochloric acid. The precipitate, which is insoluble in water, dissolves in the acid.

Pyridine, heterocyclic tertiary amine, is miscible with water in any proportion. The ionization constant of pyridine is not high ($K = 2 \times 10^{-9}$) and its aqueous solution is only slightly alkaline.

Pyridine produces readily soluble salts with one equivalent weight of acid. When hydrochloric acid, formed in the hydrolysis of ferric chloride, is bound by pyridine, the equilibrium of the reaction is shifted to the point where ferric hydroxide precipitates.

Like benzene, whose structure is similar (see Experiment 154), pyridine is stable to oxidants.

Like many aromatic hydrocarbons (Experiment 163), pyridine reacts with picric acid to give crystalline picrate, $C_5H_5N \cdot C_6H_2(NO_2)_3OH$ (m.p. 167 °C), soluble in excess pyridine.

The amine character of pyridine shows not only in that it forms salts with acids. Like many other amines, it forms compounds with tannin and some salts of heavy metals. The double salt of pyridine with mercuric chloride has the composition $C_5H_5N \cdot HgCl_2$.

242
Reactions of Quinoline

REAGENTS

Quinoline.
Picric acid, saturated solution.
Tannic acid, 10 per cent solution.
Mercuric chloride, 3-5 per cent solution.

Shake 1 ml of quinoline with 5-6 ml of water. Note the characteristic odour of quinoline. Allow the mixture to settle and decant the aqueous solution into another test tube. Use it in the tests that follow below.

Add 1-2 ml of water to the quinoline that remains in the former tube, then add concentrated hydrochloric acid, drop by drop, and shake to dissolve all quinoline. The homogeneous liquid becomes hot. Add alkali solution: droplets of free quinoline are formed.

Carry out the tests with the aqueous solution of quinoline following the instructions given for the tests with pyridine (see Experiment 241).

A. Quinoline acts on litmus paper and ferric chloride, to reveal its alkaline properties only vaguely.

B. In the reaction with potassium permanganate in an alkaline medium with heating, the colour of the permanganate quickly vanishes and manganese dioxide precipitates.

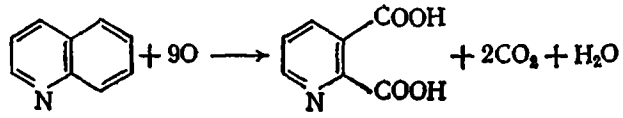
C. In the test with picric acid it immediately precipitates quinoline picrate in ample quantities.

D. Quinoline reacts with tannic acid solution to precipitate a white substance.

E. In the reaction with mercuric chloride (POISON!), quinoline gives a white precipitate.

Unlike pyridine, quinoline is only moderately soluble in cold water (about 6 g in 100 ml) and is even a weaker base ($K = 1 \times 10^{-9}$). Strong acids react with quinoline to give readily soluble salts that are decomposed by alkalis (cf. Experiment 203).

Quinoline is easily oxidized with potassium permanganate. The site of oxidation is the benzene ring of the condensed dicyclic molecule. The resultant product is dibasic 1,2-quinolinic (α, β-pyridinedicarboxylic) acid:



The character of oxidative decomposition reveals close similarity of the dicyclic systems of quinoline and naphthalene (see Experiment 183).

Quinoline reacts with picric acid, tannic acid, and mercuric chloride like pyridine. Quinoline picrate melts at 203 °C.

243
Formation of Quaternary Ammonium Derivatives of Pyridine and Quinoline

REAGENTS

Pyridine.
Quinoline.
Methyl iodide (see Experiment 28).
Ethyl iodide (see Experiment 29).
Silver oxide, moist (see Experiment 110).

A. Place a few drops (0.1-0.2 ml) of pyridine into two separate test tubes. Add an equal volume of methyl iodide into one, and ethyl iodide into the other test tube. The reaction begins spontaneously or with slightly heating the mixtures. The homogeneous mixtures turn yellow, then cloudy, and delaminate. Heavy oil first separates, and soon solidifies.

Repeat the test using quinoline instead of pyridine.

To remove an excess of free amines, wash the obtained crystals with benzene.

B. Dissolve the obtained alkyliodides of pyridine and quinoline in a small quantity of water. Add phenolphthalein and a small quantity of silver oxide, and shake (see Experiment 110). Silver iodide precipitates immediately in all cases, and the solution becomes strongly alkaline.

Being tertiary amines, pyridine and quinoline can combine with alkyl halides to give quaternary ammonium salts. Alkyl iodides are the fastest to react. They give the compounds $[C_5H_5NR]^+I^-$ and $[C_9H_7NR]^+I^-$. These compounds very readily crystallize and have characteristic melting points (in °C):

N-Methyl pyridinium iodide	118
N-Methyl quinolinium iodide	133
N-Methyl quinolinium iodide hydrate	72
N-Ethyl pyridinium iodide	90
N-Ethyl quinolinium iodide	156

Methyl iodide usually reacts faster than ethyl iodide. Alkylhalides of pyridine are colourless (when pure), whereas the derivatives of quinoline are yellow.

When treated with moist silver oxide (cf. Experiment 110) they give the corresponding quaternary bases, whose solutions react strongly alkaline.

Pyridine, quinoline, and their derivatives have been extensively studied by A. E. Chichibabin.

244
Sulphonation of Indigo

REAGENTS

Indigo, powder.

A. Place a very small quantity of indigo powder into a test tube, add 1-2 ml of water, and shake, first at room temperature and then with heating. Indigo does not dissolve in water and the aqueous layer remains colourless on standing. To prove insolubility of indigo, place a drop of its aqueous suspension on filter paper: a large colourless wet circle forms on the paper around the blue spot of the dye.

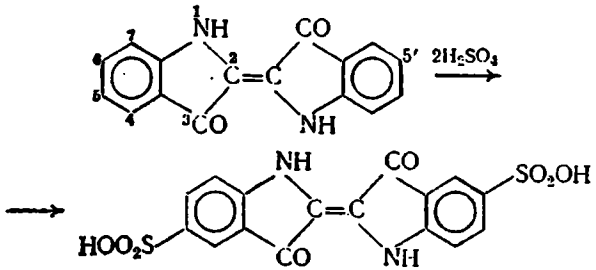
B. Place about the same quantity of indigo powder into a dry test tube and add 1 ml of concentrated sulphuric acid. Heat the blue mixture over a burner until it boils and then allow to cool. Add a few drops of the obtained liquid to 2-3 ml of cold water. A deep blue solution is produced. Place a drop of the solution on filter paper. It produces a large blue spot.

Use the prepared solution in Experiment 245.

The properties of indigo were studied by Fritzsche and Nentsky.

In the structural formulas of indigo and its derivatives that follow below the nitrogen atoms are shown in the *trans* position (on opposite sides as regards the central double bond); this complies with the results of recent investigations.

Indigo is easy to sulphonate. Two sulpho groups are attached in the 5 and 5′ positions:



Unlike the starting substance, the obtained indigotindisulphonic acid is readily soluble in water. Its disodium salt is known as indigo carmine. It is used in laboratory investigations. Indigo carmine is a less fast dye compared with indigo.

The spot test on filter paper is often used to establish completeness of dissolution of the dye or its complete isolation from solution.

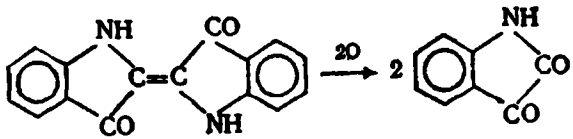
245
Oxidation of Indigo Carmine

REAGENTS

Indigo carmine, dilute solution (see Experiment 244).

Add a few drops of concentrated nitric acid to 2-3 ml of bright blue clear solution of indigo carmine. Observe the colour change in the cold and with slightly heating the mixture.

Indigo is readily oxidized by strong oxidants such as nitric or chromic acid, or hydrogen peroxide. On oxidation it gives isatin:



Indigo carmine is oxidized in these conditions to give isatinsulphonic acid.

Isatin (m.p. 203 °C) and its sulphonic acid are red in the solid state and yellow in solution form.

246
Indigo (Vat Blue 1)

REAGENTS

Indigo, powder.

Stannous chloride, 10-12 per cent solution (hydrochloric acid is added to destroy turbidity), or *sodium hydrosulphite*, powder.

A strip of white fabric.

A. Add dilute alkali to 5-6 ml of stannous chloride solution, drop by drop, to dissolve the precipitate that first falls out. Place 10-20 mg of indigo in a small mortar and grind it with 1-2 ml of water. Add a drop of the obtained suspension to the stannite solution and place the test tube into a boiling water bath. The dark blue turbid mixture very soon turns green, then pale yellow and absolutely clear.

Continue the heating and add the indigo suspension in 2-3 drop portions, each time waiting until the blue colour vanishes. A dark yellow clear liquid is formed. It may contain a small precipitate and a thin blue film at the interface (with air).

If sodium hydrosulphite is used, add at once the entire volume of indigo suspension (see above) into a test tube containing 0.1-0.2 g of hydrosulphite and 1-2 ml of water. Then add 1-2 ml of alkali

solution, shake, and heat carefully: the precipitate is quickly dissolved to give a dark yellow solution.

B. Transfer about 1 ml of the solution prepared in test A into another test tube, add 2-3 ml of water, stopper the test tube, and shake strongly. The yellow liquid soon turns blue, non-translucent, and small flakes of indigo precipitate from it.

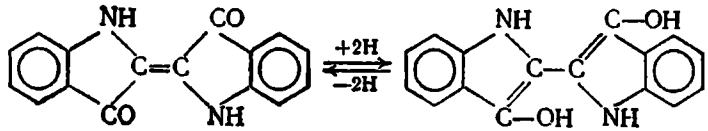
C. Wet a strip of white fabric in water, press out excess liquid, and steep it in the remaining yellow alkaline solution of the dye. Stir the fabric with a glass rod or copper wire for 1-2 minutes, then remove it from the dye, slightly press out excess liquid and hang from the same glass rod (or wire) fixed in the stand.

The fabric soon becomes green in the air, and in a few minutes a deep blue colour develops. Put the dyed fabric in running water under a tap to see whether or not the dye runs off.

Stannites of alkali metals in solution form are strong reductants:

$$SnO_2^{2-} + H_2O \longrightarrow SnO_3^{2-} + 2H$$

When reduced in an alkaline medium, indigo turns into *indigo white* (leuco indigo). It has the phenol character and is readily soluble in alkali solutions to give yellow solutions. Air rapidly re-oxidizes this product back to indigo (cf. Experiment 132).



The alkaline solution of indigo white, which is also known as vat blue, easily impregnates fabric. Re-oxidation of the adsorbed indigo white with air converts it to the insoluble indigo. Formed inside the fibres, the dye is very fast.

The common way of preparing the vat solution in industry is by sodium hydrosulphite, $Na_2S_2O_4$, which is a very strong reductant:

$$Na_2S_2O_4 + 2NaOH = 2Na_2SO_3 + 2H$$

The solution of sodium hydrosulphite is unstable, but in the dry state it keeps well.

247
Reactions of Uric Acid

REAGENTS

Uric acid.

A. Place a small quantity of uric acid into a test tube, add 2-3 ml of water, and test the acid for solubility at room temperature and with heating. Cool the mixture, add alkali solution, drop by drop,

to dissolve the acid, and then add hydrochloric acid until the solution reacts acid.

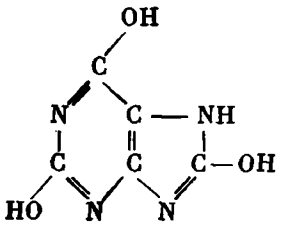
B. Mix a drop of sodium carbonate and a drop of silver nitrate on a porcelain plate (or a glass plate placed over a sheet of white paper). Add a few crystals of uric acid into the mixture and observe the change in colour of the precipitate.

C. Place a few crystals of uric acid in a porcelain dish, add 3-4 drops of concentrated nitric acid, and carefully evaporate the mixture to dryness. Evaporate in the HOOD on a sand bath or on a gauze over a burner. The dry residue in the dish turns pink-red.

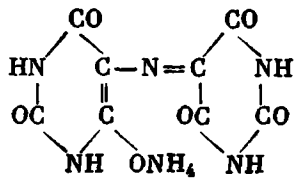
Allow the dish to cool and wet the dry residue with a drop of aqueous ammonia on one side and with a drop of dilute alkali on the other. Apply the liquids by a glass rod. Ammonia changes the pink-red colour of the residue to violet, and the alkali to bluish.

Uric acid (2,6,8-trioxypurine) is very sparingly soluble in water (1 mg in 40 litres). It is a very weak acid. Only two of its hydrogen atoms can be replaced by metal. Its acid potassium salt is sparingly soluble in water, whereas neutral potassium and also sodium salts are well soluble.

Uric acid is easy to oxidize. In test B, soda converts the acid into solution, and silver carbonate that first precipitates is reduced to black silver metal. Uric acid reacts with nitric acid to give a coloured mixture of oxidation and hydration products. Ammonia or alkali reacts with this mixture to give intensely coloured salts of purpuric acid.



Uric acid



Murexide

Purpuric acid ammonium salt, murexide, derives its name from the genus of mollusk *Murex*. The name is given because of the colour that is very much like that of the ancient purple dye (6,6′-dibromoindigo) furnished by this sea snail.

248
Reactions of Nicotine

REAGENTS

Nicotine, dilute solution.
Tannic acid, 10 per cent solution.
Picric acid, saturated solution.
Potassium mercuric iodide, solution.

To prepare the solution of potassium mercuric iodide, add, drop by drop, 5 per cent potassium iodide to 1 ml of 5 per cent mercuric chloride (nitrate), until the red precipitate, that first falls out, is all dissolved.

Use 0.5-1 ml portions of the nicotine solution in the tests that follow below. Note the specific odour of nicotine.

A. Add a drop of phenolphthalein to the solution of nicotine: it reacts alkaline.

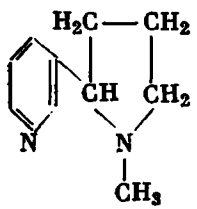
B. Add a few drops of iodine solution: red-brown substance precipitates.

C. Add tannic acid solution: a white substance precipitates.

D. Mix the nicotine solution with picric acid: a yellow substance precipitates.

E. Add a drop of dilute acetic acid and a few drops of potassium mercuric iodide to the nicotine solution: a yellowish precipitate falls out.

Like other alkaloids, nicotine is amine. Its structure is close to that of pyridine. Nicotine is actually beta-pyridyl-alpha-N-methyl-pyrrolidine:



Nicotine contains two amine nitrogen atoms, one of which is not part of the aromatic ring. It is therefore a much stronger base than pyridine (see Experiment 241).

Nicotine forms sparingly soluble addition products with iodine, tannic acid, picric acid, and salts of mercury, which is characteristic of many amines. These reactions of precipitation are common for most alkaloids.

Unlike pyridine, nicotine is readily oxidized with potassium permanganate to give nicotinic (pyridine-3-carboxylic) acid.

The presence of heterocycles containing nitrogen in the molecules of most alkaloids was first discovered by A. N. Vyshnegradsky, the pupil of A. M. Butlerov.

249
Formation of Methylene Blue

REAGENTS

para-Nitrosodimethylaniline or its *salt* (see Experiment 219).
Ammonium sulphide, 1-2 *N* solution.

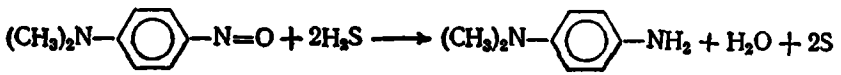
Use the HOOD.

Place 1 ml of a colourless solution of ammonium sulphide into a test tube and add a few small grains of *p*-nitrosodimethylaniline (free base or salt). Heat the mixture until it starts boiling: a yellow solution is formed. Cool the solution and carefully acidify it with dilute hydrochloric acid: hydrogen sulphide and free sulphur are liberated.

Add ferric chloride, drop by drop, to the solution turbid from precipitated sulphur. At first, there are no changes, but as ferric chloride solution is further added, the mixture turns dark blue.

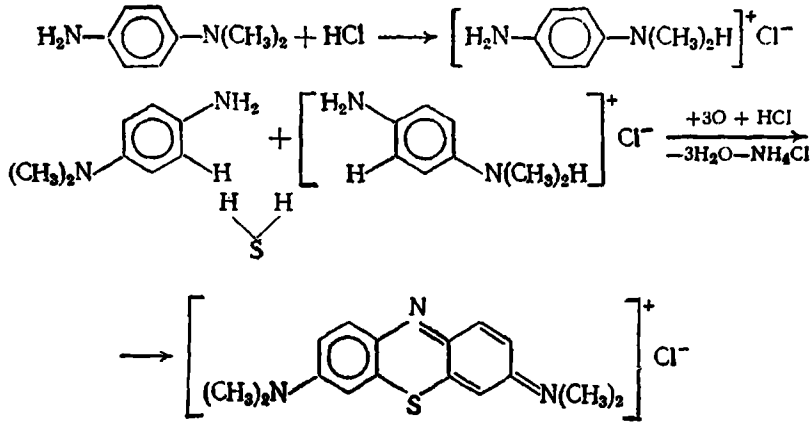
Transfer a few drops of the obtained dye solution into a beaker containing 10-20 ml of water: the liquid turns bright blue. Add alkali and glucose (see Experiments 131 and 132) or some other reductant: the blue colour vanishes.

Hydrogen sulphide in a weakly alkaline medium reduces *p*-nitrosodimethylaniline to *p*-aminodimethylaniline:

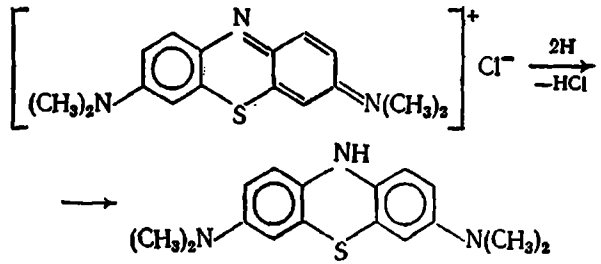


In an acid medium this diamine forms an ammonium salt that is condensed in the presence of ferric chloride (oxidant) with the second molecule of the diamine and hydrogen sulphide. The thiazine ring

is closed and methylene blue formed:



Methylene blue is reduced in an alkaline medium to a leuco base, in which the quinonoid structure is absent; the solution is therefore decolourized:



Re-oxidation of the leuco base converts it back to the dye (cf. Experiments 131 and 132).

ORGANIC COMPOUNDS CONTAINING SULPHUR

Carbon disulphide, ethyl mercaptan, methyl mustard oil, and phenyl mustard oil (see Table 16) will be used as substances containing sulphur. All these compounds, except carbon disulphide, will be prepared in the course of the experiments.

Table 16

Properties of Organic Compounds Containing Sulphur

Substance	Formula	M. p., °C	B. p., °C	Density, g/cc
Carbon disulphide	CS_2	−109	46	1.26
Ethyl mercaptan	$C_2H_5—SH$	−144	35	0.83
Methyl mustard oil	$CH_3—N=C=S$	35	119	1.07 (37 °C)
Phenyl mustard oil	$C_6H_5—N=C=S$	−21	218	1.13 (16 °C)

250
Formation of Ethyl Mercaptan

REAGENTS

Ethyl bromide (see Experiment 27).
Sodium hydrosulphide, solution.
Ethyl alcohol.

To prepare sodium hydrosulphide (NaSH) solution, mix a few drops of saturated sodium sulphide solution with 1 ml of water, add a drop of phenolphthalein, and then dilute hydrochloric acid, drop by drop, with shaking, until the red colour vanishes. Cloudiness does not interfere with the reaction.

Use the HOOD.

Place 0.5 ml of sodium hydrosulphide solution into a test tube and add 0.5 ml of alcohol and 2-3 drops of ethyl bromide. Gently heat the mixture: the penetrating garlic-like odour of ethyl mercaptan is felt.

At the end of the experiment, place the test tube containing the reaction mixture into a bath with chromic-sulphuric acid, or alkaline solution of potassium permanganate. Perform this operation in the HOOD as well.

Thioalcohols, or mercaptans, are easily formed by the action of alkyl halides on hydrosulphides of alkali metals:

$$RBr + NaSH \longrightarrow NaBr + RSH$$

Mercaptans are characterized by weak acid properties. They are much more volatile than the corresponding alcohols since their molecules are almost not associated. The specific odour of mercaptans can be sensed with as small concentrations as 1 mg per 20,000 cubic metres of air. At high concentrations the sense of smell is dulled.

Residual quantities of mercaptans should be destroyed by oxidants that convert them first to disulphides, whose odour is also unpleasant but not so strong. Further oxidation destroys the odour.

251
Formation of Xanthates

REAGENTS

Ethyl alcohol, rectified.
Carbon disulphide.

Mix 1 ml of concentrated solution of potassium hydroxide with 1 ml of alcohol. Add 0.5-1 ml of carbon disulphide and strongly shake the mixture with cooling the test tube in water. Yellow crystals of potassium xanthate are soon precipitated.

Separate part of the precipitate, dissolve in a few millilitres of water, and add 1-2 ml of copper sulphate solution. A brown precipitate that falls out quickly turns yellow.

Salts of xanthic acid, which is actually an acid ester of thiolthioncarbonic acid $RO-C\begin{matrix}\nearrow S \\ \searrow SH\end{matrix}$, are easily formed by the action of carbon disulphide and alkalis on alcohols:

$$CS_2 + ROH + NaOH \longrightarrow R-O-CS-SNa + H_2O$$

Xanthates are as a rule readily soluble in water.

Potassium ethylxanthate is relatively slightly soluble and preci-

pitates in the form of crystals. If sodium hydroxide is used instead of potassium hydroxide, the precipitate does not fall out.

In an exchange reaction with copper sulphate, potassium ethylxanthate is converted into copper ethylxanthate. A brown cupric salt is first formed. It oxidizes excess xanthate and converts into cuprous xanthate. The yellow colour of the cuprous salt gives rise to the name 'xanthate' (Greek *xanthos* yellow).

Acids easily decompose xanthates to recover alcohol. Reaction of copper sulphate with carbon disulphide and alkali, with formation of copper alkyl xanthate precipitate, is characteristic of alcohols in general (not only of ethyl alcohol). Cellulose treated with alkali and then with carbon disulphide gives cellulose xanthate solution. When forced into an acid bath through small holes, cellulose xanthate gives viscous rayon (artificial silk) (cf. Experiment 142).

Esters and salts of xanthic acids were studied in detail by L. A. Chugaev in 1895-1905. He showed that thermal decomposition of these esters produces unsaturated hydrocarbons, and used this reaction in the study of terpenes and volatile oils.

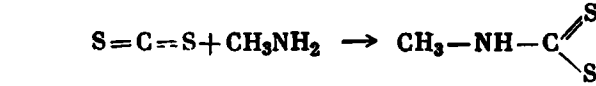
252
Formation of Methyl Mustard Oil

REAGENTS

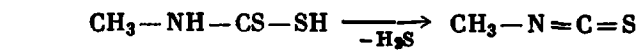
Methylamine, solution (see Experiment 114).
Carbon disulphide.
Ethyl alcohol, rectified.

Place a few millilitres of methylamine solution in a test tube and add an equal volume of alcohol and a few drops of carbon disulphide. Heat the mixture to boiling, add 1-2 ml of ferric chloride solution, and continue heating the liquid containing the precipitated black substance. Carefully feel the odour of the boiling mixture. Note the pungent acrid odour of mustard oil.

Carbon disulphide easily attaches methylamine at the double bond C=S to give an unstable methyldithiocarbamic acid:



that reacts with ferric chloride to eliminate hydrogen sulphide and to give methyl mustard oil (methyl isothiocyanate):



Hydrogen sulphide reacts with ferric chloride to precipitate black Fe_2S_3 (cf. Experiment 253).

Unlike thiocyanic acid esters, in which the radical is bonded with the sulphur atom, isothiocyanates (the esters of isothiocyanic acid, S=C=NH) contain in their molecule the hydrocarbon radical bonded to the nitrogen atom.

Isothiocyanates are known as mustard oils because of the specific odour of mustard that depends on the allyl isothiocyanate, $CH_2=CH-CH_2-NCS$, first synthesized by N. N. Zinin in 1854.

253
Preparing Phenyl Mustard Oil

REAGENTS

Carbon disulphide.
Aniline.
Lead nitrate.

Place 3 ml of carbon disulphide and 5 ml of concentrated ammonia solution into a 150-200 ml round-bottom flask. Strongly shake the flask, cool it in water, and add 3 ml of aniline in small portions. Tightly stopper the flask and shake strongly again cooling it from time to time in water. Emulsion is first formed, and then the liquid becomes homogeneous. Yellowish crystals precipitate in 5-7 minutes. Shake the flask incessantly: the reaction mixture is almost fully solidified. Cool the flask for another ten minutes, add 75 ml of water, and when the crystals dissolve, add a solution of 10 g of lead nitrate in 20 ml of water. Shake the flask energetically: the mixture strongly thickens to form a yellow precipitate that gradually blackens.

Place a few boiling stones into the flask, connect an outlet tube and a water-cooled condenser, and distil the mixture by strongly heating the flask over a burner. Collect the distillate in a small test tube containing 1 ml of dilute sulphuric acid. Distil 40-50 ml of cloudy liquid. Allow the distillate to settle, pipette the colourless heavy oil having the characteristic odour into a small dry test tube, and dry with a grain of calcium chloride.

The yield is 2-2.5 g.

The product can be used without purification in Experiment 254.

254
Reactions of Phenyl Mustard Oil

REAGENTS

Phenyl mustard oil (see Experiment 253).
Aniline.
Mercuric oxide, yellow.
Ethyl alcohol, crude or rectified.

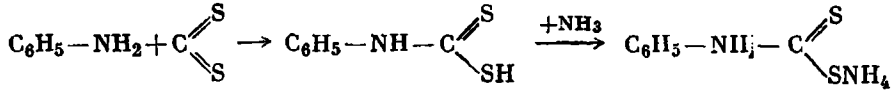
A. Dissolve 0.5 ml of phenyl mustard oil in 1.5 ml of alcohol, add 1.5 ml of concentrated ammonia solution, and heat gently. The liquid first delaminates and then becomes homogeneous. Cool the test tube in water, and in 5-10 minutes, if the mixture remains clear, shake it. White crystals of phenylthiourea precipitate. It can be re-crystallized from hot water. The melting point is 154 °C.

B. Mix a few drops of phenyl mustard oil with an equal volume of aniline and heat slightly. The mixture is then heated spontaneously and solidified on rubbing with a rod. The formed diphenylthiourea can be re-crystallized from alcohol. The melting point is 153 °C.

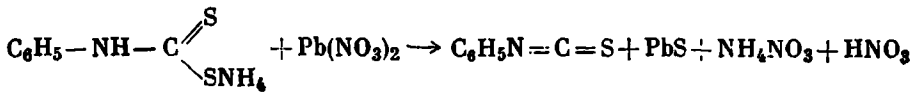
C. Use the HOOD.

Place a small quantity of mercuric oxide in a dry test tube, add a few drops of phenyl mustard oil, and heat the mixture until it starts boiling. Move the burner aside: the mixture is now heated spontaneously, the precipitate blackens, and the liquid boils. A pungent irritating odour of phenyl isocyanate is felt.

Carbon disulphide easily enters into addition reactions (cf. Experiments 251 and 252). It reacts with aniline and ammonia to give an ammonium salt of phenyldithiocarbamic acid:

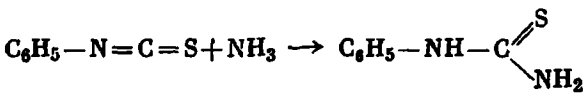


that is obtained in crystal form in Experiment 253. Lead nitrate first isolates an insoluble lead salt of the same acid, and heating eliminates an atom of sulphur to give phenyl isothiocyanate (phenyl mustard oil). The summary equation of the reaction is as follows:



Salts of copper, zinc, or iron can be used instead of the lead salt.

Phenyl mustard oil easily combines with ammonia (Experiment 254, A) to give phenylthiourea:



(To prevent this reaction, during distillation of phenyl mustard oil in Experiment 253, sulphuric acid is placed in the receptacle to bind ammonia.)

Phenyl mustard oil reacts with excess aniline (Experiment 254, B) to give symmetrical diphenylthiourea (thiocarbanilide), $C_6H_5NH-\underset{\underset{S}{\|}}{C}-NHC_6H_5$. This compound is quite stable. It is also

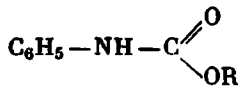
prepared by the direct reaction of aniline with carbon disulphide (with elimination of hydrogen sulphide). Thiocarbanilide is used as flotation agent in concentrating sulphide ore and in the manufacture of rubber curing accelerators.

Thiocarbanilide reacts with hydrochloric acid with boiling to eliminate a molecule of aniline and to give back phenyl mustard oil.

Phenyl mustard oil reacts with mercuric oxide to replace the sulphur atom in the isothiocyanate molecule by oxygen and to give a more volatile phenylisocyanate:

$$C_6H_5-N=C=S+HgO \longrightarrow HgS+C_6H_5-N=C=O$$

Phenylisocyanate (b.p. 164 °C) has a pungent irritating odour and like phenyl mustard oil reacts with amines to give urea derivatives, and also with alcohols and phenols to give phenylurethanes:



which are esters of phenylcarbamic acid.

EXPERIMENTS WITH ORGANOMAGNESIUM COMPOUNDS

Organomagnesium compounds are formed in the course of the experiments as intermediate products and should immediately be used in further reactions.

255
Preparing Benzoic Acid

REAGENTS

Magnesium metal.
Ethyl ether, absolute.
Iodine.
Bromobenzene (see Experiment 151).
Carbon dioxide.

Magnesium is used in the form of turnings or a ribbon cleaned with an abrasive material.

Wash ethyl ether with a 2 per cent solution of ferrous sulphate, dry with calcium chloride, and then keep for a few hours over metallic sodium (in a bottle closed with a calcium chloride tube) until hydrogen bubbling stops. Collect the needed quantity of the ether using a dry pipette without disturbing the precipitated flakes.

Obtain carbon dioxide from a cylinder provided with a reducing valve, or from a Kipp generator, and dry it by passing through a calcium chloride absorption tube. It is very convenient to place pieces of dry ice (solid carbon dioxide) into the reaction mixture instead of gaseous CO_2. Before adding dry ice, wash it with absolute ether to remove water condensed on its surfaces.

Carry out the reaction in a long-neck flask with a cold finger reflux condenser fitted in the plug provided with a hole (Fig. 3). Place 0.7 g of magnesium, 10 ml of ether, 3.3 ml (5 g) of bromobenzene, and a small crystal of iodine into a dry flask, fix a condenser, and slightly heat the flask on a water bath. If the reagents and the apparatus are dry, the reaction begins in a few seconds: the solution gets cloudy, the colour of iodine vanishes, and ether starts boiling.

Replace the warm water bath by a dish with cold water and adjust the reaction rate so that the ether boils quietly. At the end of the reaction (in 10-15 minutes) heat the flask again in warm water until magnesium is all dissolved. Cool the flask in a mixture of snow and salt, dismantle the condenser, and place a carbon dioxide delivery tube instead. The tube should freely enter the flask and almost reach its bottom. Continue the cooling (to minus 10-15 °C) and pass carbon dioxide into the mixture for 15 minutes. Pass the gas at a rate of 3-4 bubbles per second. If solid carbon dioxide is used, add 10-12 g. Shake the flask at short intervals. The reaction mixture is soon separated into two layers.

Discontinue CO_2 delivery, add 10 g of snow (ice) into the flask, and then add concentrated hydrochloric acid, drop by drop with shaking, to dissolve the precipitate. Transfer the flask contents into a separatory funnel and discharge the two layers into two separate beakers. Place the lower layer back into the funnel. add 5 ml of ether, and shake several times. Discharge the lower aqueous layer and discard it. Shake the joined ether solutions in the funnel first with 25 ml of dilute sodium hydroxide solution, and then (after separation of the alkaline solution) with 10 ml of water. Mix the aqueous extract with the alkaline solution and add concentrated hydrochloric acid dropwise until the solution reacts clearly acid to congo (see Experiment 75). Separate precipitated crystals of benzoic acid with suction in 10-15 minutes, wash with cold water, press out excess liquid, and dry. The yield is about 2 g.

To purify the product, re-crystallize the acid from water (see Experiment 1).

The ether solution (remaining after separation of benzoic acid with alkali and water washing) can be evaporated to dryness on a water bath, and the obtained diphenyl, re-crystallized from a water-alcohol mixture (see Experiment 2). The melting point of diphenyl is 70 °C.

256
Preparing tert-Amyl Alcohol (2-Methyl-2-butanol).

REAGENTS

Magnesium metal.
Ethyl ether, absolute.
Iodine.
Ethyl bromide.
Acetone, anhydrous.

Ethyl bromide should be dried with calcium chloride, and acetone with calcined potassium carbonate (see Experiment 3). For preparing magnesium and ether, see Experiment 255.

Carry out the experiment in a long-neck flask having the capacity of 50-100 ml, and provided with an outlet tube (Fig. 9), to which a calcium chloride absorption tube is connected. A reflux condenser should be fitted in a tight stopper and inserted into the flask as low as possible.

Place 1 g of magnesium, 10 ml of ether, 3.1 ml (4.4 g) of ethyl bromide, and a small crystal of iodine into a dry flask. If the reaction does not spontaneously begin in 1-2 minutes (see Experiment 255), gently heat the flask on a warm water bath. If boiling is too vigorous, cool the flask in cold water so that the ether boils quietly. In 10-15 minutes magnesium is almost all dissolved.

Cool the flask in a mixture of snow and salt to a temperature of minus 10-15 °C, disconnect for a moment the calcium chloride tube, and add, in small portions, a mixture of 2.9 ml (2.3 g) of acetone with 5 ml of ether, also cooled to minus 10-15 °C. Add the mixture by a pipette and shake the flask energetically. The reaction is vigorous. A white dense precipitate is formed. As soon as acetone is all added, put aside the cooling bath and heat the flask in warm water until the ether gently boils for 15 minutes. Cool the flask with water, dismantle the condenser and the calcium chloride tube, add 10 g of snow or ice into the flask, and then add about 5 ml of cold concentrated hydrochloric acid. Add it carefully in small portions with strongly shaking until the precipitate is dissolved. Avoid adding excess acid.

The flask contents are separated into two (sometimes three) layers. Transfer the reaction mixture into a separatory funnel. Pass the lower aqueous layer into a separate vessel. Transfer the upper layer (or two layers) into a flask. Extract the aqueous layer twice with 3-5 ml portions of ether. Add the extracts to the upper layer and drop a few pieces of dry potash into the joined extract. When liberation of carbon dioxide discontinues, stopper the flask with a plug provided with a calcium chloride tube and allow the reaction mixture to stand for a few hours. The ether solution clarifies and becomes homogeneous.

Transfer the solution in portions into a test tube provided with a thermometer and a long outlet tube, and distil ether on a water bath into a receptacle cooled with water and ice. Distil the brown remainder by heating the test tube over a burner. tert-Amyl alcohol is distilled within the temperature range of 99-102 °C (after distillation of a small intermediate fraction that boils out at 60-90 °C).

The yield is 1-1.5 g. The odour of the product is characteristic of tertiary alcohols.

257
Preparing Triphenylcarbinol

REAGENTS

Magnesium metal.
Ethyl ether, absolute.
Iodine.
Bromobenzene (see Experiment 151).
Ethyl benzoate (see Experiment 192).

Carry out the reaction in a flask provided with an outlet tube and a reflux condenser (see Experiment 256). Connect a calcium chloride tube to the outlet tube.

Place 0.65 g of magnesium, 2.7 ml of bromobenzene, a crystal of iodine, and 10 ml of ether into a dry flask. Control the reaction rate by heating and cooling the flask contents in water (see Experiment 255). The resultant product is an ether solution of phenylmagnesium bromide. When almost all magnesium has been dissolved cool the flask in water, disconnect the calcium chloride tube, and add by a pipette through the outlet tube, 1.5 ml of dry ethyl benzoate in 5 ml of ether. Add it in small portions and with shaking the flask. Allow the coloured reaction mixture to stand for 10-20 minutes (with shaking at intervals), then dismantle the condenser, and add 10-15 g of crushed ice into the flask. Basic salts of magnesium precipitate. Dissolve them by carefully adding dilute hydrochloric acid.

Allow the mixture to settle, collect the lower aqueous layer by a pipette, and discard. Add 20 ml of water and a boiling stone to the ether layer, close the flask with a stopper, connect a water-cooled condenser, and distil ether on a water bath. Put aside the bath, wipe the flask dry, and continue the distillation over a burner. Collect the distillate in test tubes. Excess bromobenzene and the side product diphenyl are distilled with steam. Discontinue the distillation when heavy drops stop separating in a distillate sample. Add 10 ml of cold water to the still residue. The heavy yellow oil collected on the bottom solidifies. Separate the product with suction, press out excess liquid on the funnel, and then dry in filter paper. The yield is 1.5-1.8 g.

White crystals of triphenylcarbinol can be used without purification in Experiments 236 and 237.

Whenever higher purity is required, re-crystallize the carbinol from alcohol or benzene. The product melts at 164 °C.

Organometallics are substances whose molecules contain a metal atom bonded directly to a carbon atom. Very many metals are known at the present time to form such organometallic compounds.

Most fatty, alicyclic, and aromatic monohalogen-substituted hydrocarbons can react with magnesium to give organomagnesium compounds according to the following general equation:

$$R{-}X + Mg \longrightarrow R{-}Mg - X$$

where X is a chlorine, bromine, or iodine atom.

The reaction is given the name of Grignard (1901). It proceeds smoothly at room temperature only in the presence of ethers or tertiary amines that react with the resultant products to give complex compounds such as $C_2H_5MgBr \cdot 2(C_2H_5)_2O$. The compounds usually dissolve in excess ether.

The above equation describes the formation of only organomagnesium compounds of the type R—Mg—X. Three reaction products are actually equilibrated simultaneously in the ether solution:

$$2RMgX \rightleftharpoons R_2Mg + MgX_2$$

The easiness with which alkyl halides react with magnesium decreases in the following series: alkyl iodides, alkyl bromides, alkyl chlorides. The reaction is usually accelerated in the presence of free iodine.

Organomagnesium compounds are very reactive and easily attach themselves across the bonds C=O, C≡N, etc. The formed products when decomposed with water give a basic salt of magnesium and an organic compound, whose structure is far more complicate than that of the starting substance. The structure of the compounds thus obtained can be accurately controlled by the researcher, and this fact accounts for the wide use of organomagnesium compounds in synthesis.

The bond C—Mg in organomagnesium compounds is strongly polarized. In many cases an organomagnesium compound reacts in the form of carbanion R^- that is produced by the elimination of cation MgX^+. Carbanion is a nucleophile and it is attacked by electrophilic agents, e.g. the proton of water (see Experiment 258). Some reactions of these substances can, however, be regarded as radical.

The action of carbon dioxide on organomagnesium compounds (see Experiment 255) gives carboxylic acids:

$$RMgX + C(=O)(=O) \longrightarrow R-C(=O)-OMgX \xrightarrow{+H_2O} R-C(=O)-OH + Mg(OH)X$$

This method was used by N. D. Zelinsky in 1902 for preparing benzoic acid. The scientist used it as the demonstration experiment.

Organomagnesium compounds react with ketones (see Experiment 256) to give tertiary alcohols:

$$RMgX + R'R''C{=}O \longrightarrow RR'R''C{=}OMgX \xrightarrow{H_2O} RR'R''C{-}OH + Mg(OH)X$$

With aldehydes they react in the same way to give secondary alcohols. If esters are introduced into the reaction, ketones are usually obtained, and in some cases esters react consecutively with two molecules of the organomagnesium compound. The final product of the reaction is a tertiary alcohol. For example, triphenylcarbinol is formed as follows (see Experiment 257):

$$\begin{matrix} C_6H_5 \\ C_2H_5O \end{matrix}\!\!>\!C{=}O \xrightarrow{+C_6H_5MgBr} (C_6H_5)_2C\!\!<\!\!\begin{matrix} OC_2H_5 \\ OMgBr \end{matrix} \xrightarrow[-C_2H_5OMgBr]{+C_6H_5MgBr}$$

$$\longrightarrow (C_6H_5)_3C{-}OMgBr \xrightarrow[-Mg(OH)Br]{+H_2O} (C_6H_5)_3C{-}OH$$

Magnesium bromide alcoholate, which is produced simultaneously, is also decomposed with water to give alcohol and a basic salt of magnesium. For the sake of convenience of isolation of the reaction product, insoluble basic salts of magnesium are dissolved by adding hydrochloric acid:

$$2Mg(OH)Br + 2HCl \longrightarrow 2H_2O + MgCl_2 + MgBr_2$$

In the process of preparing and using organomagnesium compounds, they react with excess starting halogen derivative to give side products, mainly hydrocarbons. For example, in the process of preparing phenylmagnesium bromide (Experiments 255 and 257), small quantities of diphenyl are formed:

$$C_6H_5MgBr + C_6H_5Br \longrightarrow MgBr_2 + C_6H_5{-}C_6H_5$$

Operations with organomagnesium compounds (till the moment of their final decomposition with water) should be carried out in the absence of moisture, since water retards the reaction and energetically decomposes alkyl (aryl) magnesium halides with formation of hydrocarbons.

The reaction is used for analytical purposes (see Experiment 258).

At the same time, absolute ether is very hygroscopic. The ether solutions used in Experiments 256, 257, and 258 should therefore be protected from atmospheric moisture with guard tubes packed with calcium chloride (see Chapter 1). The simpler and quicker Experiment 255 can be performed without such guard tubes, but the use of absolute ether is obligatory.

258
Determining the Number of Active Hydrogen Atoms in Organic Compounds (Chugaev-Zerevitinov-Terentiev Method)

REAGENTS

Magnesium metal.
Ethyl ether, absolute.
Iodine.
Methyl iodide or *ethyl iodide* (*bromide*), see Experiments 27, 28, and 29.
Any pure *anhydrous organic substance containing hydroxyl or carboxyl groups* (*butyl* or *amyl alcohol*, *hydroquinone*, *benzoic acid*, etc.).
For preparing magnesium and ether, see Experiment 255.

Prepare a solution of methylmagnesium iodide or ethylmagnesium bromide (iodide) in a long test tube closed with a stopper provided with a calcium chloride tube. Place 10 ml of ether, 0.3-0.4 g of magnesium, 1 ml of alkyl halide, and a crystal of iodine into the test tube, and shake: if the test tube and the reagents are dry the reaction soon begins. Lower the test tube in cold water to control the reaction rate so that the ether only gently boils. When spontaneous evolution of heat stops, allow the reaction mixture to stand for ten minutes, then add 10 ml of ether, and allow to settle. Residual quantities of magnesium and flakes precipitate to the bottom.

Determine active hydrogen in a wide test tube provided with a side arm (Fig. 1). Close the test tube with a rubber plug and connect a soft rubber tubing to the side arm. The other end of the rubber tubing should have a glass tube bent into a hook. Measure the volume of the liberated gas by a 100-ml measuring cylinder, filled with water and overturned into a water jar. Fix the cylinder in the ring of the stand.

Place a piece of glass wool onto the bottom of the reaction test tube and thoroughly dry it by blowing hot air. Weigh out a sample of the substance in question on an analytical balance using a small test tube, 10 mm in diameter and 50-70 mm long, manufactured from a glass tubing. The sample tube should freely enter the reaction test tube. (As the smaller tube is arranged concentrically with the larger one, the gap should be at least 5-7 mm.) The mass of the sample should be about 0.1-0.2 g. Add 1-2 ml of ether and carefully shake to dissolve the sample.

Using a pipette, place 5-6 ml of an organomagnesium compound into the reaction test tube, and then carefully insert the sample tube containing the test substance into the reaction test tube. The level

of the solution in the reactor should be 1-2 cm below the upper edge of the test tube. Tightly stopper the reactor, lower it in the vertical position into a water bath (e.g. into a desiccator without a lid), fix in the stand clamp, and leave for 5-10 minutes. The temperature of water in the bath should be 15-18 °C. Put the end of the bent outlet tube into the measuring cylinder filled with water from beneath, immerse the reactor into water, and turn it slowly so that the liquids could quietly mix. The side arm of the reactor should be pointed upwards.

Gas is intensively liberated. Carefully shake and turn the reactor in water so that the liquids could better mix. The gas evolution stops in 1-2 minutes and the meniscus of water in the bent tube begins moving slowly towards the reactor. Remove the reactor, lower the cylinder into a water jar, and align the liquid levels inside and outside the reactor. Record the volume of gas in the cylinder (V, ml).

The number of active hydrogen atoms in a molecule of the test substance (H_a) can be found from the formula:

$$H_a = \frac{MV}{24{,}000 \times m}$$

where M is the molecular mass of the substance in question, V is the volume of the liberated gas, and m is the mass of the sample.

Organomagnesium compounds react with hydroxyl-containing substances to give hydrogen and magnesium halide alcoholate:

$$ROH + IMgCH_3 \longrightarrow CH_4 + ROMgI$$

Gaseous hydrocarbon (methane or ethane) is liberated in our Experiment. Its volume can be measured, and the quantity of a substance containing hydroxyl, or the number of hydroxyl groups contained in its molecule, can be determined. The method was suggested by L. A. Chugaev in 1902 and developed in more detail by F. V. Zerevitinov in 1907-1914. A. P. Terentiev improved the method (1940-1950). More complicate apparatus and methods are used for accurate measurements, and corrections for temperature, atmospheric pressure, and the pressure of water vapour are incorporated in the calculations.

The results obtained in the described simplified conditions of the experiment are only tentative, but the quantity of the active hydrogens in a molecule of a substance (1, 2 or 3) can be determined to a high degree of certainty. A mole of active hydrogen gives 22,400 ml of gaseous hydrocarbon at 0 °C and a pressure of 760 mm Hg. At 15-18 °C, this volume is about 24,000 ml. The method can be used for determining active hydrogen atoms in hydroxyl, carboxyl, sulphhydryl and amino groups in various organic compounds. The

method is also applicable for determining water of crystallization in crystal hydrates and unbound water in inert substances in which it is contained as admixture.

It should be noted that water reacts with organomagnesium compounds through the agency of both its hydrogen atoms:

$$2RMgX + H_2O = 2RH + MgX_2 + MgO$$

The presence of traces of water in the apparatus or in the test substance therefore strongly distorts the results of the determination.

CHAPTER TWENTY

SYNTHETIC POLYMERS

Industrial plastics, such as polymethyl methacrylate and polystyrene, will be used in some experiments in this chapter. They may be in the sheet form or in the form of some articles, such as buttons, tooth-brush handles (polymethyl methacrylate), parts of electric (especially high-frequency) apparatus (polystyrene). These materials, or fragments of former articles should be preliminarily crushed to 5-7 mm particles (using a hammer or cutters). Transparent or almost transparent material should be used since otherwise mistakes in the selection of the material are possible. The colour of the material almost does not matter since the monomers obtained by depolymerization (methyl methacrylate and styrene) can be purified by repeated distillation.

Substances that have already been used in the previous experiments, such as formaldehyde (neutralized, see Chapter 7), phenol, hexamethylenetetramine, urea, aniline, glycerol, phthalic anhydride, and dichloroethane, will also be required in the experiments of this chapter.

Polymers are high-molecular substances whose giant molecules have been composed by the union of many simple molecules (monomers) in the process known as *addition polymerization*, which is actually the union of molecules without elimination of any particles of different character. If the monomer molecules are united in a macromolecule with liberation of water, ammonia, or some other substances, the process is called *polycondensation* (*condensation polymerization*).

The high-molecular synthetic substances that will be used in our experiments, such as polymethyl methacrylate, polymethacrylic acid, and polystyrene, are obtained by the addition polymerization process, while the others are prepared by the condensation polymerization. Some polymers are described as thermoplastics. When heated they soften and on cooling set again without changing their

other properties. These are, for example, polystyrene, novolaks, etc. Other plastics are thermosetting, i.e. when heated they change irreversibly their properties, and usually become infusible and insoluble (thermoset) materials. A-stage resins (resols), amino (aniline) resins, and urea-formaldehyde resins represent such plastics.

Natural polymers, proteins, polysaccharides, and also their synthetic derivatives (for instance, cellulose acetate) are discussed in Chapters 11 and 21.

259
Preparing Methyl Methacrylate (Depolymerization of Polymethyl Methacrylate)

REAGENTS

Polymethyl methacrylate (Plexiglas).

Place 5-6 g of crushed polymer into a test tube and stopper it tightly using a plug with an outlet tube. Connect the latter with a 25-30 cm long condenser tube and lower its other end into a receptacle almost to its bottom. Cool the receptacle (test tube) with water and snow. Heat the polymer in the test tube over a burner, first carefully and then stronger, moving the flame of the burner around the test tube. The polymer grains fuse and gradually volatilize. Continue the heating until the polymer is almost all volatilized. A yellowish liquid is collected in the receptacle. The yield of crude monomer is 90-95 per cent of the polymer mass.

To purify the monomer, distil it. Its greater part is distilled at 98-101 °C. Try the attitude of methyl methacrylate to the reagents for the double bond (see Experiments 18 and 19).

Use the obtained methyl methacrylate in Experiments 260, 261, and 262.

The high-boiling fraction contains the dimer and trimer of methyl methacrylate.

260
Polymerization of Methyl Methacrylate

REAGENTS

Methyl methacrylate, distilled (see Experiment 259).
Benzoyl peroxide, or 25-30 per cent *hydrogen peroxide*.

If benzoyl peroxide is not available in the laboratory, dissolve 1 g of sodium hydroxide in 8 ml of water in a flask or a wide test tube, and cool the solution in a cooling mixture to 0 to —5 °C (thermometer in solution). Add drop by drop with shaking, first 2.5 ml

of hydrogen peroxide and then 2 ml of benzoyl chloride. The temperature of the liquid should not rise above +1 °C. Continue shaking the test tube: crystals of benzoyl peroxide precipitate. Separate them with suction, wash with water, dry in air (without heating), and use in the experiments.

The equation of the reaction is as follows:

$$2C_6H_5COCl + H_2O_2 + 2NaOH = 2NaCl + 2H_2O + C_6H_5COOOCOC_6H_5$$

The melting point of benzoyl peroxide is 104 °C. Like most peroxides, it is unstable. Explosions from detonation and heat are occasionally reported. Therefore, handle it with care and do not prepare in large quantities.

Place 2-3 ml of methyl methacrylate in a test tube, add a few grains of dry benzoyl peroxide, and shake to dissolve them. Place the test tube into a water bath with a thermometer, heat to 80-90 °C, and shake periodically. Viscosity of the mixture increases appreciably in 10-20 minutes, and in 40-50 minutes from the beginning of the heating process the mixture becomes very thick and almost non-fluid. Remove the test tube from water, wipe dry, and slightly heat over a burner to remove residual monomer. Allow the test tube to cool.

The solid translucent column of the obtained polymer can be removed from the test tube by breaking the latter. Sometimes the polymer happens to drop from the test tube on slightly tapping it against a table.

Try the small grains of the obtained polymer for solubility in benzene or chloroform. Try also for combustibility by holding the polymer with tongs in the flame of the burner.

If benzoyl peroxide is absent, hydrogen peroxide can be used instead. Add about 2-3 drops per millilitre of the monomer. The polymerization reaction proceeds at a much slower rate and strong heating with shaking the mixture is required.

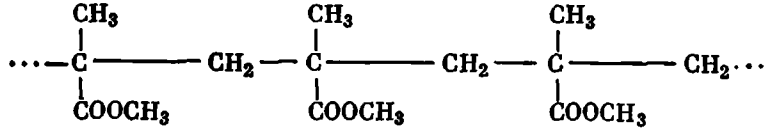
Methyl methacrylate, $H_2C=C(CH_3)—COOCH_3$, is a colourless liquid appreciably soluble in water and having a pleasant etherial odour; its density is 0.94 g/cc. In industry it is usually manufactured from acetone through alpha-hydroxyisobutyronitrile (acetone cyanhydrin).

Methyl methacrylate reacts with potassium permanganate and soda to give a clear reaction for the double bond, but adds bromine very slowly. On standing, methyl methacrylate polymerizes spontaneously, presumably because of the formation of peroxidic compounds with atmospheric oxygen, which catalyse the polymerization reaction (cf. Experiment 44). To prevent polymerization, an inhibitor of oxidation (hydroquinone) is usually added to the technical product. The inhibitor remains partly in the polymer and partly

passes back into the monomer on depolymerization. To accelerate polymerization and to withstand the inhibiting action of hydroquinone, one of the best catalysts of polymerization, benzoyl peroxide, is used in Experiment 260 (as well as in industry). Benzoyl peroxide is easily dissolved in methyl methacrylate.

Esters of methacrylic acid, like free acid (see Experiment 263), are polymerized by the homolytic reaction through formation of free radicals. The donor of radicals for the construction of the polymer chain is peroxide (see explanations to Experiments 18, 44, and 181). For example, benzoyl peroxide easily falls into free radicals $C_6H_5COO\cdot$. Such a radical unites with one of the carbons at the double bond, whereas the unpaired electron appears at the second of these carbons. The new free radical initiates a new chain whose growth is very fast till the moment when the chain is broken by another growing chain or by some other reason. The inhibitor (in our case hydroquinone) binds free radicals and controls the growth of the chain. The higher the concentration of benzoyl peroxide in the monomer, the faster is the polymerization rate at a given temperature. Hydrogen peroxide is sparingly soluble in the monomer, and the polymerization with this peroxide is therefore much slower.

Polymethyl methacrylate (Plexiglas) is a very valuable plastic material. Unlike common silicate glass, it is permeable to ultraviolet radiation. The molecular mass of the polymer is of the order of 100,000-200,000, i.e. its particles consist of 1000-2000 structural units (residues of the monomer molecules) that are united into long chains:



When heated to a temperature of 100 °C polymethyl methacrylate begins softening, and at 250-300 °C it is almost completely depolymerized. It easily burns in the flame of a burner and produces first a blue and then luminous flame without soot and without melting (in contrast to polystyrene; see Experiment 265). The burning is accompanied with slight cracking. The polymer is absolutely insoluble in water and sinks (unlike the starting monomer; see above). It follows that as the monomer is converted into the polymer the spatial arrangement of particles is consolidated. Polymethyl methacrylate swells in benzene and chloroform, but dissolves in them very slowly and incompletely.

Other esters of methacrylic acid also give transparent polymers, but they are softer than polymethyl methacrylate.

261
Emulsion Polymerization of Methyl Methacrylate

REAGENTS

Methyl methacrylate (see Experiment 259).
Ammonium persulphate.

Dissolve 0.4-0.5 g of ammonium persulphate in 10 ml of water and divide the clear solution into two approximately equal portions.

A. Add about 0.5 ml of methyl methacrylate to one portion and shake: an unstable and quickly segregating emulsion is formed.

B. Add 0.5-1 ml of methyl methacrylate to the other portion of the solution, and add with shaking 2-3 ml of alcohol to obtain a homogeneous solution.

Place both test tubes into a hot (70-80 °C) water bath. Strongly shake the test tube A at short intervals. In a few minutes a very stable milk-white emulsion is formed. It does not segregate on standing, and the layer of methyl methacrylate, which first rises to the surface, gradually disappears. Meanwhile the liquid in the test tube B becomes only slightly turbid, but semi-transparent drops of resin are deposited on its walls and the bottom. Heat the test tubes for 15-20 minutes (seeing to it that the mixture in the test tube B does not boil out), then put them in the stand, and allow to cool.

Add an equal volume of water and a few drops of concentrated hydrochloric acid to the thick emulsion in the test tube A. The emulsion quickly (quicker with heating) decomposes and the coagulate aggregates into heavy drops or flakes on shaking.

White flakes that form small solid grains of the polymer are gradually produced in the test tube B (in addition to the thick resin) on shaking.

When extracted from the mother liquor by a rod, the resin becomes brittle in a few hours and can easily be ground into powder.

Ammonium persulphate, $(NH_4)_2S_2O_8$, contains the —O—O—group, i.e. it is a peroxide, and catalyses the polymerization of methyl methacrylate. It is very convenient to use it in polymerization in aqueous emulsions and solutions. This method is often used in industry. The obtained insoluble granular polymer is used in the manufacture of various products by hot moulding under pressure.

Polymerization in a homogeneous medium (test tube B) is much faster. The obtained polymer first contains admixtures of the monomer (that can easily be detected by the odour) and is therefore plastic. The monomer is then volatilized.

262
Preparing Methacrylic Acid and Its Properties

REAGENTS

Methyl methacrylate (see Experiment 259).
Ethyl alcohol, crude or rectified.
Benzoyl peroxide (see Experiment 260).
Congo test papers (see Experiment 75).

Mix in a test tube 2 ml of methyl methacrylate, 1 ml of alcohol, and 4 ml of concentrated sodium hydroxide solution. Shake the mixture: it soon becomes homogeneous and markedly hot.

Transfer the obtained solution in 15-20 minutes into a small dish and evaporate almost to dryness on a gauze over a burner. To prevent overheating and burning, continually stir the solution with a rod. Then allow the dish to cool, and add, with stirring, a few millilitres of dilute (3 : 1) hydrochloric acid, adding it in small portions until the congo test paper turns blue (see Experiment 75). Transfer the liquid containing a small precipitate into a test tube and allow to settle. Methacrylic acid rises to the surface as oily liquid having specific odour. Pipette it carefully and transfer into a dry test tube. The yield is about 1 g.

Try the obtained product for the attitude to cooling in a mixture of water with snow or ice. Dissolve a few drops of methacrylic acid in 1-2 ml of water and test with reagents for the double bond (see Experiments 18 and 19).

The obtained product can be used without purification in Experiment 263.

Methacrylic acid can be distilled without preliminary drying. It boils at 160 °C.

263
Polymerization of Methacrylic Acid

REAGENTS

Methacrylic acid (see Experiment 262).
Hydrogen peroxide, 25-30 per cent solution.
Benzoyl peroxide (see Experiment 260).
Ammonium persulphate.

Divide methacrylic acid prepared in Experiment 262 into three equal portions and place in three separate test tubes (A, B, and C). Add an equal volume of hydrogen peroxide into test tube A, a few grains of benzoyl peroxide into test tube B, and 3 ml of water and

0.05-0.1 g of ammonium persulphate into test tube C. Place the test tubes in hot (80-90 °C) water.

Shake test tube A: the mixture gradually homogenizes and in 5-20 minutes turns into a soft transparent resin that becomes opaque and solid on cooling.

Benzoyl peroxide grains quickly dissolve in test tube B. Very soon the liquid suddenly (sometimes with a sharp sound) turns into a thick white mass.

White flakes are formed in test tube C in a few minutes. On further heating and shaking they aggregate into a resin clot that sinks to the bottom and becomes transparent.

Allow the test tubes to cool, test the obtained polymerizates with caustic alkali solution with heating for solubility, and also try the action of excess hydrochloric acid on this alkaline solution.

Methyl methacrylate easily hydrolyses in alkali solutions, the hydrolysis products (methyl alcohol and methacrylate) passing into the aqueous solution:

$$CH_2=\underset{\displaystyle CH_3}{\overset{|}{C}}-COOCH_3+NaOH \longrightarrow CH_3OH+CH_2=\underset{\displaystyle CH_3}{\overset{|}{C}}-COONa$$

Ethyl alcohol is added to facilitate dissolution of the starting ether and to accelerate hydrolysis.

Methacrylic acid (density 1.01 g/cc) is well soluble in water, but is easily salted out and rises to the surface over the saturated solution of sodium chloride (see Experiment 262). It is polymerized much easier than its ester (cf. Experiment 260), and together with the other products of polymerization forms the octamer $(C_4H_6O_2)_8$. Methylacrylic acid reacts very quickly and clearly with reagents for the double bond.

When cooled to 0 °C, methacrylic acid quickly solidifies. The pure product melts at 16 °C. Sometimes the acid polymerizes spontaneously. It also polymerizes when dried with sodium sulphate or calcium chloride.

Polymethacrylic acid contains the groups

$$\cdots-CH_2-\underset{\displaystyle COOH}{\overset{CH_3}{\overset{|}{C}}}-CH_2-\underset{\displaystyle COOH}{\overset{CH_3}{\overset{|}{C}}}-\cdots$$

in its chain macromolecules and can be esterified directly in the polymer state to form polymethyl methacrylate. This polymer, in turn, hydrolyses to give polymethacrylic acid also without any intermediate monomers. The polymers are only sparingly soluble and their reaction with other substances is therefore very slow.

Some salts of polymethacrylic acid (like of many other insoluble acids) are well soluble in water.

Polymethacrylic acid is used in industry in the manufacture of some composite plastics.

264
Preparing Styrene (Depolymerization of Polystyrene)

REAGENTS

Polystyrene, 5-7 mm particles.

Carry out the depolymerization of polystyrene as in the case with polymethyl methacrylate (see Experiment 259). Since the boiling point of styrene is higher than that of methyl methacrylate (145 °C), the condenser tube is not required, and it will be sufficient to lower the outlet tube of the reaction test tube almost to the bottom of a receptacle cooled with water. It is not necessary to add snow into the cooling water either. It is recommended that the upper part of the reaction test tube and the bent part of the outlet tube should be wrapped with asbestos.

Polystyrene softens on heating and flows to the bottom of the test tube. Discontinue the heating when polystyrene residue turns into a thick black liquid.

The yield of yellowish distillate in the receptacle is about 75-85 per cent of the polystyrene mass. Almost colourless pure styrene can be isolated from the distillate by another distillation, collecting the fraction boiling out at 140-145 °C. The yield of the fraction is about 50 per cent of the mass of the starting polystyrene.

Test the styrene with the reagents for the double bond (see Experiments 18 and 19).

The obtained styrene can be used in Experiments 152 and 265.

Styrene is insoluble in water and has a specific odour (resembling that of toluene, xylene, and many other lower homologues of benzene). Its density is 0.91 g/cc.

265
Polymerization of Styrene

REAGENTS

Styrene, purified by distillation (see Experiment 264).
Benzoyl peroxide (see Experiment 260), or *hydrogen peroxide*, 25-30 per cent solution.
Benzene.

A. Place 3-4 ml of styrene and a few grains of benzoyl peroxide into a test tube and shake: the peroxide dissolves. Place the test

tube containing the liquid on a sand bath (on the surface of the sand) and gently boil for 25-35 minutes. The liquid becomes very thick. Remove the test tube from the bath, hold it horizontally, and slightly heat in the flame of the burner to remove the residual monomer. Sometimes its vapour can catch fire at the test tube mouth and burn with a smoky flame.

As the test tube is cooled, the transparent polymer fully solidifies. The polymer well adheres to glass, and as it shrinks on cooling, the test tube and the polymer itself may crack.

B. Remove the obtained polymer from the test tube and dissolve part of it in 1-2 ml of benzene with heating. Transfer half the obtained solution onto a watch glass. A transparent film remains on the glass after evaporation of the solvent. The film is easy to detach after keeping under water for 1-2 minutes.

Add 1-2 ml of alcohol to the remaining portion of the benzene solution. Add the alcohol in small portions: the polymer precipitates from the solution as a white sticky resin. It can be removed by a glass rod and pressed into a ball. The resin is very elastic, but on exposure to air it gradually becomes brittle and falls into powder.

Hydrogen peroxide can be used in Test A instead of benzoyl peroxide. Then add about 2-3 drops of the peroxide per millilitre of the monomer. The polymerization rate is somewhat slower in this case and the mixture strongly foams on heating. To prevent bumping, shake the test tube at short intervals. As the test tube is further heated, not only the remaining monomer but also water of the hydrogen peroxide solution are removed from the thickened mixture.

Styrene (phenylethylene) is an unsaturated hydrocarbon; it gives clear reactions for the double bond (see also Experiment 152). The usual method of preparing styrene in industry is by dehydrogenation of ethylbenzene whose vapour is passed over a catalyst heated to 550-600 °C:

$$C_6H_5CH_2CH_3 \longrightarrow C_6H_5CH{=}CH_2 + H_2$$

To prevent spontaneous polymerization during storage, a small quantity of hydroquinone should be added to technical styrene. Polymerization of styrene into polystyrene is accelerated by peroxide (see explanations to Experiment 260). Thus initiated polymerization has the radical mechanism. In industry styrene is also polymerized with acid catalysts. In this case the reaction is the ionic type and the polymer has slightly different, more valuable properties.

The reaction of styrene polymerization is exothermic. The formed polymolecules have the molecular mass of the order of 30,000-

300,000, and contain the structural units

$$\cdots -CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-\cdots$$

Unlike polymethyl methacrylate, they are not linear but branched. For this reason, during depolymerization of polystyrene, not only the monomer and the lower styrene polymers, but hydrocarbons of other type, e.g. 1,2-diphenylethane, 1,3-diphenylpropane, are formed as well. The yield of the monomer is therefore much lower than in depolymerization of polymethyl methacrylate (cf. Experiment 259), and the residue in the reaction test tube is a complex mixture of various reaction products.

Polystyrene is inflammable. Unlike polymethyl methacrylate it burns with a bright strongly smoky flame. The hot part of the burning sample becomes soft and can be drawn into fibres. The melting point of polystyrene depends on the process by which the polymer is obtained and varies within a wide range, from 90 to 250 °C. At 300 °C depolymerization occurs. In contrast to the monomer, polystyrene is heavier than water (see Experiment 260). On storage, polystyrene sometimes becomes covered with cracks and turns nontransparent. It is readily soluble in benzene and chloroform. A film is formed on drying of such solutions. The adhesion of the film to glass is high but when water is applied, it wettens the glass and the film is easy to detach (cf. Experiment 146). Polystyrene is insoluble in alcohol. The polymer isolated from benzene by adding alcohol contains benzene that can be detected by odour. Benzene is gradually evaporated on storage.

Polystyrene is relatively thermally unstable, but it is highly resistant to water and frost, and is a very efficient electric insulator. In this respect it is inferior only to mica. Hence its wide use in electrical industry. At the present time its use has been extended to the manufacture of various structures and building materials.

266
Formation of Phenol-Formaldehyde Resin by Condensation of Phenol with Formaldehyde

REAGENTS

Phenol.
Formaldehyde, 35-40 per cent solution.

A. Place 2.5 g of phenol, 5 ml of formaldehyde, a boiling stone into a test tube and heat the mixture to obtain a homogeneous liquid. Gently boil for 1-2 minutes. Add by a pipette 0.2-0.3 ml of con-

centrated hydrochloric acid and shake: the hot mixture keeps boiling without external heating. In 1-2 minutes, the liquid becomes cloudy, and a heavy non-transparent gradually thickening oil is separated. If the liquid stops boiling, heat it over a burner for 1-2 minutes. Decant the upper turbid aqueous layer and add approximately an equal volume of water. Boil again for 1-2 minutes, decant water, and transfer the resin together with remaining water on a watch glass. Cool the pale lilac elastic resin, remove it from the glass, dry in filter paper, and press into a small ball. During storage the resin gradually hardens and becomes brittle. The longer the boiling, the faster the ageing process.

B. Proceed as instructed in Test A, except that instead of hydrochloric acid, add 1.5 ml of concentrated ammonia solution to a a slightly cooled mixture of phenol and formaldehyde. The resin thus obtained is transparent, but the process of its polymerization is slower and the yield lower than in Test A. The resin is brown-yellow.

If the reaction mixture in Tests A and B is heated for an insufficiently long time, the resin obtained is sticky and almost does not solidify.

Test the obtained resins for solubility in dilute alkali (with heating) and in alcohol.

C. Heat part of the resin prepared in Tests A and B in a dry test tube holding it horizontally. Excess water is removed from the starting materials (that form a liquid distillate) and the main bulk of the resin melts. Stop heating: the molten resin solidifies into a compact transparent mass. If the heating is continued, the resin foams and solidifies into a porous mass. On further heating, the formed product does not melt but chars.

Cool the test tube and try the obtained product for solubility in alcohol and in alkaline solution with boiling.

267
Formation of Phenol-Formaldehyde Resin from Phenol and Hexamethylenetetramine

REAGENTS

Phenol.
Hexamethylenetetramine.
Alcohol, rectified or crude.

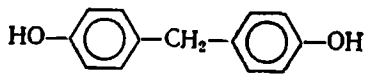
Place 2.5 g of phenol and 0.5 g of hexamethylenetetramine into a test tube, add a boiling stone, and carefully heat the mixture over a burner. A homogeneous liquid is first formed, and then it begins

bubbling to liberate gas. The quiet bubbling continues when the heating is suspended. Carefully smell the odour of the liberated gas. Shake the test tube at short intervals: the liquid gradually thickens. When the gas evolution stops, heat the test tube slightly again and pour the greater part of its contents onto a cold glazed tile, glass plate, or a piece of glossy paper. On cooling the yellow transparent resin becomes brittle. Try its small samples for solubility in alcohol and alkali solution. Convert part of the resin into an infusible product by heating (see Experiment 266, C).

Add 1-2 ml of alcohol to the remaining part of the resin and boil the mixture to dissolve the resin. Pour the obtained yellow thick solution onto a flat glass plate in a thin layer. The resin is soon dried. Carefully heat part of the dry novolak from beneath over a burner for a few minutes seeing to it that it does not char. Cool the plate and compare the hardness of the heated and non-heated parts of the film.

Phenol quickly reacts with formaldehyde in solution only in the presence of a catalyst (acids or alkalis), and the course of the process (electrophilic replacement of hydrogen in the ortho and para positions; see explanations to experiments of Chapter 13) largely depends on the character of the catalyst.

In the presence of acids, one molecule of formaldehyde is condensed with two molecules of phenol with elimination of water to give *p,p'*-dihydroxydiphenylmethane:

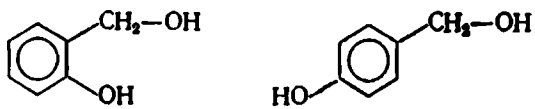


that reacts with an excess of the same substances to give a novolak. The latter contains macromolecules of various structure, e.g. structures with the groups

$$\cdots - C_6H_3(OH) - CH_2 - C_6H_3(OH) - CH_2 - \cdots$$

Similar resins can be obtained with replacement of phenol by its homologues. The molecular mass of such resins is comparatively small (below 2000). They are fusible materials soluble in organic solvents and alkali solutions.

In the reaction of phenol with formaldehyde in the presence of alkali, the first reaction products are mainly isomeric hydroxybenzyl alcohols:



that are further condensed with elimination of water to give resols (A-stage resins), which differ from novolaks by the presence in their macromolecules of the groups $-CH_2OH$ at the benzene nuclei. Novolak resin can therefore react with excess formaldehyde to give resol, which in turn can react with excess phenol to convert back into a novolak resin. Like novolaks, resols are fusible polymers well soluble in organic solvents. When heated to 150-160 °C, resols are converted into resites by cross-linking, i.e. by formation of linkage between linear macromolecules. The cross-linking is effected through the methylene groups $-CH_2-$ that are formed by elimination of water with the participation of the $-CH_2OH$ groups of resol. Resites have the three-dimensional structure and their molecular mass is higher than that of resols. Resites are therefore infusible and insoluble.

In Experiment 266, A, formaldehyde is taken in excess with respect to phenol. The formed novolak resin can therefore, on heating, give resol and finally resite (see above).

The solubility of the products of these reactions in alcohol indicates the presence of linear medium-size macromolecules, and the solubility in alkali solutions points to the presence of free phenol hydroxyl groups.

Cross-linking of molecules into resites is much accelerated in the presence of alkaline catalysts. Ammonia that is added to the reaction mixture (see Experiment 266, B) is first bound with formaldehyde (cf. Experiment 64). As the latter is bound with phenol, ammonia is liberated (cf. Experiment 65) to function as the alkaline catalyst, whereas its excess is gradually volatilized. If the reaction is effected with another alkali catalyst (sodium hydroxide), the reaction products remain in solution for a long time, and are precipitated only on prolonged boiling.

In Experiment 267, hexamethylenetetramine furnishes both formaldehyde and ammonia. The formaldehyde to phenol ratio in this experiment is by far lower than in Experiment 266, B, but the continuous supply of the alkaline catalyst (ammonia) ensures quick formation of both resol and resite. Resites produced with hexamethylenetetramine contain certain quantities (3-4 per cent) of bound nitrogen. It is quite probable that the benzene rings of macromolecules in such resites are linked not only through the $-CH_2-$ and $-CH_2OCH_2$ groups, but through groups $-CH_2-NH-CH_2-$ as well.

If the catalyst is added to the mixture of phenol and formaldehyde in the quantity greatly exceeding that specified in Experiments 266, A and B, infusible and insoluble products are very quickly produced. They are almost useless for practical purposes.

In industry phenol-formaldehyde resins are usually manufactured in two stages (as described in the above experiments). Phenol or

its homologues first give resols or novolaks, which are (either pure or with fillers) then converted into insoluble and infusible products by hot moulding under pressure. The properties of such materials depend on the filler used. The names of plastics vary accordingly: Textolite (with textile fabric), Faolite (asbestos and sand), etc. Bakelites and carbolites are usually manufactured with wood flour, or the filler is absent at all.

J. F. Baeyer was the first to discover the formation of resins by the action of phenols on formaldehyde (1872 in Germany), but the resins were considered unwanted reaction products at that time. And it was only in 1907-1909 that Baekeland (USA), who was engaged in the search of a synthetic substitutes for natural resin, shellac, developed a method of preparing phenol-formaldehyde. (Bakelite is thus associated with the name of this scientist.) When strongly heated, phenol-formaldehyde resins are charred, and phenol and formaldehyde can be detected in the volatile products of decomposition of the resin.

268
Condensation of Urea with Formaldehyde

REAGENTS

Urea.
Formaldehyde, 35-40 per cent neutral solution.
Oxalic acid, saturated solution.

A. Place 2 g of urea, 8 ml of formaldehyde, 1 ml of concentrated ammonia solution, and a boiling stone into a test tube, and fix it in the stand in the inclined position (in the HOOD). Heat the test tube over a burner and boil its contents for 10-15 minutes to reduce the liquid volume by 1/3. Discontinue heating, allow the thickened liquid to cool slightly, and transfer half of the solution into another test tube. Add 2-3 drops of oxalic acid into the second test tube.

Mix well the contents in both test tubes by shaking and keep them on a water bath (50-60 °C) for 5-10 minutes. During this time the contents of one test tube usually vitrifies into a transparent or white mass. Cool the test tubes, add 3-4 ml of water, and compare the solubility of the products at room temperature and with heating.

The insoluble vitreous product of condensation can be removed from the test tube by breaking the latter.

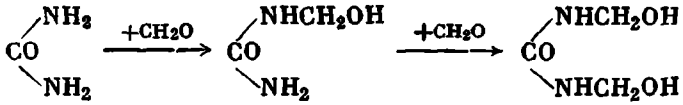
B. Carefully heat a mixture of 2 g of urea and 3 ml of formaldehyde in a test tube over a burner to dissolve urea. Transfer part of the solution into two other test tubes. One of them should contain a drop of concentrated hydrochloric acid, and the other 2-3 drops

of oxalic acid solution. Observe the changes. Heat the remaining part of the solution until it starts boiling and also note the changes in the appearance of the mixture.

C. Place 1 g of urea, 1.5 ml of formaldehyde, and 10 ml of water in a test tube and shake the mixture to dissolve urea. Transfer half of the obtained solution into another test tube, add 0.5 ml of concentrated hydrochloric acid, shake, and keep both test tubes on a hot water bath for a few minutes. Note the different behaviour of the test tube contents.

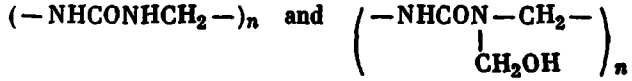
Test the obtained white product for solubility in boiling water.

The character and the rate of the reaction between urea and formaldehyde in an aqueous solution depend on the reaction conditions. In the presence of alkalis and excess formaldehyde, urea gives predominantly monomethylol and dimethylol urea:

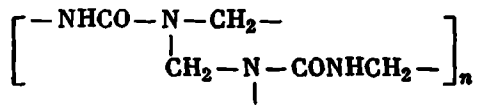


Ammonia is also an alkaline catalyst (see explanations to Experiments 266 and 267).

Methylol ureas containing hydroxyl groups are soluble in water to give viscous solutions. Heating of such solutions condenses the molecules of methylol ureas with elimination of water and formation of linear macromolecules having the structural units:



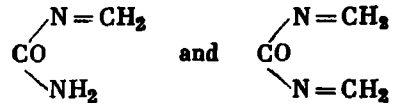
Next formed are more complicate cross-linked macromolecules with methylene links:



or cyclic molecules, presumably with 6- and 8-membered cycles. Because of their enlarged and complicated molecules and the absence of hydroxyl groups, these polymers are insoluble in water. In industry such a deepened condensation is attained by heating the dry product with a filler (for instance, wood flour) in a mould under pressure. Linear polymers soften and then set again to convert into thermosetting colourless or white urea-formaldehyde resins (carbamide or amino resins). Similar conversion in our experiment can also be attained with acid catalysts. The hardness of the end products depends on the intensity of heating of the reaction mixture.

If the reaction between urea and formaldehyde proceeds from the very beginning in the presence of an acid catalyst (for instance,

if formaldehyde is not neutralized), the first reaction products, even in dilute solutions, are predominantly water-insoluble methylene ureas:



that are polymerized immediately. The obtained product does not contain hydroxyl groups, has very large macromolecules, and is insoluble in water.

In the absence of catalysts, urea reacts with formaldehyde in dilute solutions (Test C) very slowly; the reaction in concentrated solution (Test B) is faster and liberates much heat that accounts for boiling of the mixture even when the source of external heat is removed. The condensation proceeds simultaneously in several directions but the products insoluble in water are formed slowly.

269
Condensation of Aniline with Formaldehyde

REAGENTS

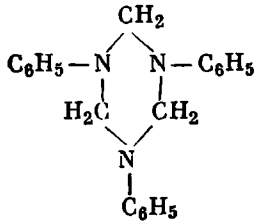
Aniline.
Formaldehyde, 30-40 per cent neutral solution.

A. Prepare 5-7 ml of aniline water (see Experiment 204) and divide it into equal portions in two test tubes. Add a drop of hydrochloric acid into one test tube and 3-5 drops of formaldehyde into both test tubes. Fix them in the stand, and compare the appearances of the reaction mixtures in 5-10 minutes.

B. Place 1 ml of aniline into a test tube, add 2 ml of water, and then hydrochloric acid, drop by drop, until aniline is all dissolved (see Experiment 203). Add an equal volume of formaldehyde and shake. The reaction begins immediately and much heat is liberated. The red insoluble reaction product does not melt on heating.

C. Mix in a test tube 1 ml of aniline, 1 ml of formaldehyde, and 0.2 ml of glacial acetic acid. Strongly shake the mixture for 1-2 minutes. The reaction begins immediately. Discard the liquid in 3-5 minutes and dry well the obtained resin in filter paper. Place the coarse-granular product in a dry test tube, add 3-5 drops of glacial acetic acid, drop a boiling stone, and heat the mixture over a burner for 4-5 minutes. The resin foams vigorously and then quietly melts. Transfer the obtained clear melt into a beaker containing cold water: it solidifies into a hard clear yellow resin.

The character of the reaction between aniline and formaldehyde depends on the reaction conditions. In the absence of acid catalysts (one test tube in Test A) a colourless methylene aniline, $(C_6H_5N{=}CH_2)_3$, is formed with elimination of water. By its structure it is triphenylhexahydrotriazine (m.p. 143 °C):



In a weakly acid medium, formaldehyde combines with aniline to form the groups CH_2OH both at the nitrogen atom and at the carbons of the benzene nucleus. When heated, such 'methylol anilines' are easily condensed with elimination of water (cf. Experiment 268) to give gradually longer chain macromolecules of various structures (Test C). A fusible resin is obtained as a result (cf. Experiment 266). In the presence of strong acids (Test B and the second test tube in Test A), such linear macromolecules are quickly linked through the groups $-CH_2-$, and the coloured reaction products having two- and three-dimensional structure turn into infusible and insoluble products (cf. Experiment 266). When these resins are heated strongly, aniline vapour can be detected in the volatile products of their decomposition.

Aniline-formaldehyde resin is less often used in the manufacture of plastics since similar phenol-formaldehyde resins (see Experiments 266 and 267) are much cheaper.

Technical formaldehyde can contain free formic acid, and formaldehyde prepared from paraformaldehyde can also contain free sulphuric acid (see the beginning of Chapter 7). If non-neutralized formaldehyde is used in the above experiments, formic acid affects the reaction course like acetic acid (Test C), and the effect of sulphuric acid is similar to that produced by hydrochloric acid (Test B).

270
Preparing Alkyd (Glyptal) Resin

REAGENTS

Phthalic anhydride, or *phthalic acid.*
Glycerol.
Alcohol or *acetone.*

Place 2 g of phthalic anhydride, 0.5-1 ml of glycerol (using a pipette made out of a glass tube without narrowing to the end), and a boiling stone into a test tube. Fix it in the inclined position in the stand,

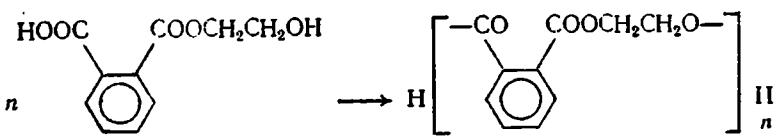
heat over a burner, and keep the mixture boiling (by intensifying the heating) for 6-10 minutes. The liquid in the test tube gradually thickens and turns yellow. The evolving vapour smells of acrolein. Therefore boil the mixture in the HOOD.

Take 1-2 drop samples using a glass rod at 2-3 minute intervals and place them on a glass or a porcelain plate. When the boiling is discontinued, transfer the hot thick liquid from the test tube onto the same plate where it solidifies. Compare the consistency and stickiness of the intermediate samples and the main bulk of the resin.

Add 2-3 ml of alcohol or acetone to the resin residue in the test tube and test the resin for solubility at room temperature and with boiling.

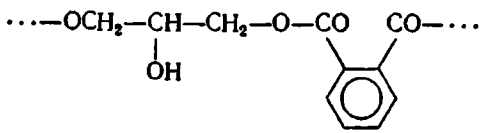
Phthalic acid can be used in the experiment instead of phthalic anhydride. The reaction mixture should then be heated for a longer time to remove the greater quantity of water.

Esterification of phthalic acid (or its anhydride) with monohydric alcohols gives common monomeric acid or neutral esters (cf. Experiment 193). Phthalic acid reacts with polyhydric alcohols to give acid esters that can then condense into long linear macromolecules. The anhydride reacts faster than the acid in this case too. For example, the reaction with ethylene glycol proceeds as follows:



Such polyesters form a hard resin that softens on heating. They are used in the manufacture of some varnishes.

When heated with glycerol, phthalic acid first forms a similar linear polyester which is a soft resin soluble in alcohol and chloroform. On further heating (above 160 °C) the linear macromolecules are gradually cross-linked through free hydroxyl groups of glycerol residues in the structural units



and also through carboxyl groups of phthalic acid taken in excess, or else the terminal groups —COOH of the formed chain acid polyesters. Water is eliminated in this process, and new (crosswise with

respect to the axes of the linear macromolecules) ester bonds are formed. A rigid three-dimensional cross-linked structure is thus formed, the molecules of which are much larger, and the resultant alkyd resin, known also as glyptalic resin, does not soften on heating. Phthalic acid reacts with other polyhydric alcohols in a similar way. Alkyd resins are relatively brittle and sparingly soluble. They are used in industry mostly in the form of their copolymers with unsaturated acids of fatty vegetable oils or rosin, or else with urea-formaldehyde resins. They are widely used in the paint industry. Paints prepared on the basis of alkyd resins give valuable protective and decorative coatings on metals, wood, etc.

The properties of alkyd resins depend on the ratio of glycerol to phthalic anhydride (acid) in the starting mixture and on the duration of the boiling process: the smaller the glycerol to phthalic anhydride ratio and the longer the boiling, the more hard and brittle and less soluble the resin obtained. If the resin is rapidly cooled inside the test tube, the latter can break because of the considerable shrinkage of the resin whose adhesion to glass is quite strong.

Alkyd resins are easily hydrolysed by alkalis and acids with heating.

271
Preparing Thiokol A (Polyethylene Polysulphide)

REAGENTS

Sodium sulphide, crystalline or saturated solution (about 18 per cent solution that may be formed on storage of the deliquescent crystals).

Sulphur, fine powder (sulphur flowers).

Dichloroethane.

Soap, high grade.

Place 50 ml of water into a flask or a beaker, add 3.5 g of crystalline sodium sulphide (or 20 ml of its saturated solution), and drop a boiling stone. Heat the mixture to boiling, add 5 g of sulphur powder, and continue boiling for another 5-7 minutes (the main bulk of sulphur dissolves). Pass the solution quickly through a pleated filter into a 250-ml long-neck flask.

Simultaneously prepare a solution of emulsifier by boiling a piece of soap (the size of a wheat grain) in 2-3 ml of water. Add the soap solution to the red-brown filtrate (polysulphide), measure the temperature of the mixture, and adjust it to 70-75 °C. Now strongly shake the flask and add in small portions (within 5 minutes) 5 ml of dichloroethane (measured out preliminarily into a separate test

tube). The liquid foams and yellow flakes precipitate. Shake the flask continually and strongly and measure the temperature of the liquid from time to time. Maintain the specified temperature by cooling or heating the mixture.

When dichloroethane is all added, shake the reaction mixture for 3-5 minutes, then cool, allow the precipitate to settle, and decant the greater part of the solution. Add an equal volume of cold water to the remaining mixture, then add a few drops of phenolphthalein and dilute hydrochloric acid to remove the red colour of the liquid. Add 1-2 ml of the acid in excess. Shake the mixture for a few minutes and allow it to stand. Discard the semitransparent milky liquid, remove the greyish sponge-like thiokol from the flask, press it well with fingers, wash in running water, dry in filter paper, and weigh. The yield is 4-5 g. Note the appearance, odour, and consistency of the material obtained. Compare the consistency of thiokol after separation from the mother solution and after a prolonged pressing with fingers.

A variety of polysulphide synthetic rubbers, classified as thiokols, are prepared by condensation of polysulphides of sodium or calcium with chlorinated hydrocarbons and fatty ethers, containing in their molecule not less than two chlorine atoms.

The polysulphide of sodium that is most suitable for the reaction with dichloroethane is sodium tetrasulphide. It can be prepared by adding the precalculated quantity of powdered sulphur to a hot aqueous solution of sodium sulphide:

$$Na_2S + 3S = Na_2S_4$$

The colour intensity of a polysulphide solution grows with the amount of sulphur contained in it. The solution of Na_2S is colourless, Na_2S_2 yellow, and of Na_2S_4 orange-red.

The equation of the reaction in which sodium tetrasulphide is condensed with dichloroethane is as follows:

$$n\text{Na}_2\text{S}_4 + (n+1)\text{ClCH}_2\text{CH}_2\text{Cl} \longrightarrow \text{Cl}\left[-\text{CH}_2\text{CH}_2\text{S}-\underset{\underset{\text{S}}{\|}}{\text{S}}-\underset{\underset{\text{S}}{\|}}{\text{S}}-\right]_n\text{CH}_2\text{CH}_2\text{Cl} + 2n\text{NaCl}$$

The reaction is exothermic but is effected only at the interface of the aqueous solution and dichloroethane since the latter is practically insoluble in water. To accelerate the process, the mixture is heated to the temperature at which dichloroethane almost boils, and an emulsifier (soap; cf. Experiment 103) or a catalyst (oxide or hydroxide of magnesium or zinc) is added.

Solutions of sodium sulphide or polysulphide are hydrolysed and therefore react strongly alkaline. A considerable part of the terminal atoms of chlorine in the long chain molecules of the polymer are therefore saponified and replaced by the hydroxyl groups.

Part of lateral atoms of sulphur can be eliminated in the reaction, or later, during storage of the finished product, to impair the material elasticity. Sodium chloride that is formed in the reaction remains in solution, while the polymer containing a small quantity of free sulphur is isolated as droplets to give a colloid solution, latex. On acidification, latex is coagulated and thiokol particles stick together in a clot.

The simplest polysulphide rubber, thiokol A (produced from dichloroethane and sodium tetrasulphide), is characterized by a a specific, very unpleasant and stable adour that persists in goods manufactured out of this material.

Thiokol elasticity increases during its mechanical treatment (even by pressing with the fingers).

Thiokols are cheap. Although they are inferior to many synthetic rubbers with respect to their mechanical parameters, their other valuable properties are very important. They are hardly permeable to gas and vapour, very stable to solvents, such as gasoline, kerosene, and oils. Their resistance to light and air is also excellent. Thiokols are used in the manufacture of oil and petrol suction and discharge hoses, gaskets for pipe-lines and containers, etc.

The synthesis of polysulphide rubbers was developed by N. D. Zelinsky in Moscow. In 1933 he suggested these rubbers for use in rubber industry.

CHAPTER TWENTY ONE

PROTEINS

Natural and readily available products should be used in studying properties and specific reactions of proteins. Protein solutions freshly prepared for the experiment should preferably be used.

A. *Egg protein.* Mix the white of a hen's egg (about 25 ml) with 100-200 ml of distilled water in a 300-400 ml flask or a bottle by shaking vigorously. Pass the mixture through a wetted piece of cotton fabric placed in the funnel. The ends of the fabric should freely fold on the sides of the funnel without hanging from the edge. Fabric, from which the finishing size has been removed by washing, may only be used for the purpose.

An opalescing solution of egg albumin, containing a small quantity of globulin, is soon passed through the filter. The main bulk of the egg globulin, and also clots and films remain on the filter.

Use the albumin solution in the tests that follow below.

B. *Meat protein.* 1. Place 25 g of minced fresh lean meat and 50 ml of water in a beaker. Allow the mixture to stand for 20-30 minutes with stirring and then transfer it onto a funnel with a pleated paper filter. A solution of albumin containing globulin is soon filtered out. Though the solution is coloured with blood pigments, it is not an obstacle to its use.

2. Wash the meat remaining on the filter two or three times with water and press out the liquid well. Discard the washings. Transfer the bleached muscle fibres into a beaker and add 15 per cent ammonium chloride solution (60-70 ml). Stir the mixture with a glass rod at short intervals for 30-40 minutes. Transfer the mixture on a dry pleated filter. The filtration is now slow. Use the myosin solution in the experiments. When diluted with water it becomes cloudy and myosin precipitates.

C. *Milk protein.* 1. Mix 50 ml of water with 50 ml of milk and then add, with stirring, 0.2-0.5 ml of concentrated acetic acid, drop by drop, until flakes precipitate. In 5-10 minutes pass the mixture

through a cotton fabric filter (see para A). The filtration process is quick. To prepare a clear solution, pass the first turbid portions of the filtrate through the fabric again. The slightly yellowish clear solution contains albumin, part of milk globulin, and also milk sugar (see Experiment 136).

2. The residue on the filter, having the consistency of thick sour cream, consists mainly of casein mixed with fat. To prepare casein solution, add 1 ml of alkali to this residue (or to 5-6 g of curd ground with 10-15 ml of water in a mortar). Slightly grind the mixture in a mortar, add water to make a total of 25-30 ml, and pass through a pleated paper filter well wetted with water. The first cloudy portions of the filtrate should be filtered again. Fat drops are retained on the filter.

3. A solution of milk albumin (containing lactose, milk sugar) can also be prepared by adding an equal volume of saturated ammonium sulphate solution to fresh milk. Casein and globulin flakes precipitate and trap fat. Pass the mixture through a pleated paper filter. The process is quick, and the filtrate is clear. It gives all albumin reactions.

D. *Vegetable albumin.* Mix 25 g of wheat flour with 100 ml of water and allow it to stand for 30-40 minutes with jolting at short intervals. Transfer the mixture onto a large pleated filter in a funnel. Filter the first cloudy portions of the filtrate again. The filtration is rather quick. The obtained 60-70 ml of clear solution contain mainly leukosin, the albumin of wheat grains.

E. *Gelatin.* Dissolve 1 g of gelatin in 100 ml of water and add 0.5 ml of 5 per cent sodium hydroxide solution.

The experiments that follow below should preferably be carried out simultaneously with several solutions of various proteins. The solutions keep for a few days. The fastest to degrade (in 2-3 days at room temperature) is an aqueous extract of meat. A drop of toluene can retard the decay of protein solutions.

Myosin and casein solutions have the highest concentration of protein. The most dilute protein solutions are those of leukosin and water-soluble proteins of milk.

Alkaline solution of proteins (casein, gelatin) intended for Experiments 276 and 281 should first be carefully neutralized by adding dilute acetic acid until a slight opalescence develops (casein), or a litmus test paper turns pink (gelatin). In the other experiments the alkaline solutions of proteins can be used without neutralization (see also Experiment 272). A gelatin solution free from alkali should be used in Experiments 273 and 274.

272
Attitude of Proteins to Acid and Alkali

REAGENTS

Proteins, solutions.
Ammonium sulphate, 15 per cent solution.

Place 2-3 ml of a protein solution into a test tube and add, drop by drop, concentrated acetic acid with shaking. Protein precipitates in the form of a white cloudiness or flakes in all test solutions except gelatin. Add the acid in excess: the protein precipitate dissolves.

Divide the obtained acid solution into two parts. Heat one to boiling. Unlike in the starting solution (see Experiment 277) the protein is not coagulated. Add 1-2 drops of ammonium sulphate solution to the hot acid liquid: the protein coagulates.

Carefully add, drop by drop with shaking, dilute alkali solution to the other part of the acid protein solution. As the acid is gradually neutralized, the protein precipitates. In excess of alkali the protein is dissolved again. Add 1-2 ml of alkali solution and heat the liquid to boiling: the protein does not coagulate.

If the protein solution is not very strongly diluted, ammonia and hydrogen sulphide are eliminated during boiling in the presence of excess alkali (see Experiment 286).

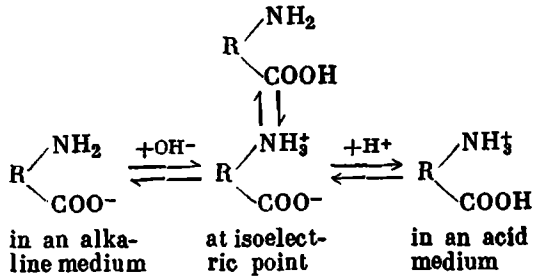
Proteins are colloid amphoteric electrolytes. Their basic properties depend on the presence of amine nitrogen, and the acid properties, mainly on the carboxyl groups:

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-; \qquad RCOOH \rightleftharpoons RCOO^- + H^+$$

In most cases the dissociation constant of protein as an acid is slightly higher than the dissociation constant of the same protein as a base. The particle of pure protein in aqueous solution is therefore usually charged negatively. As such a solution is gradually acidified, the acid dissociation of protein decreases (effect of excess H^+ ions), while the degree of the basic dissociation increases (binding of OH^- ions), i.e. the negative charge on the particles decreases and then fully disappears. As the particles lose their charge, the colloid solution of protein is made less stable and protein coagulates. The concentration of hydrogen ion in a solution, corresponding to this *isoelectric point*, is a constant characterizing a given protein. Isoelectric points of proteins used in the above experiment are within the range of pH 4.5-6.5.

Adding excess acid, i.e. lowering the pH below the isoelectric point, sharply intensifies the dissociation of protein as a base. The protein particles become positively charged, and the colloid solution

is stabilized again. On the contrary, the stability of negatively charged colloid particles of protein increases in the presence of excess alkali.



273
Gelatin Coagulation with Alcohol

REAGENTS

Gelatin, alkali-free solution.
Ethyl alcohol, rectified.

Place 5 ml of gelatin solution into three separate test tubes. Add 0.5 ml of dilute hydrochloric acid into the first and 0.5-1 ml of dilute alkali into the third test tube. Then add 10 ml of alcohol into all the three test tubes and shake.

Protein coagulates only in the second test tube, into which neither acid nor alkali was added.

Colloid particles of most proteins are hydrophilic, i.e. they are stabilized not only by the charge but by hydrate membranes as well. Gelatin is hydrated in solution to a higher extent than the other protein used in the experiment. It is not therefore enough only to remove the charge from gelatin particles (by attaining the isoelectric point) (see Experiment 272). Alcohol energetically binds water (see Experiment 38) and dehydrates the colloid particles of proteins, gelatin in particular. If the charge on the particles having no hydrate membranes is insignificant (i.e. in the vicinity of the isoelectric point), the protein coagulates. The charge on the gelatin particles in a strongly acid or alkaline medium is much higher and the particles are therefore so stable that the dehydration with alcohol does not produce coagulation.

Using buffer solutions of various pH it is possible to determine the isoelectric point to a greater accuracy. For gelatin it lies within the range of pH from 4.7 to 5.0.

274
Buffer Properties of Protein Solution

REAGENTS

Egg protein or *gelatin*, alkali-free solutions.

A. Place 3 ml of distilled water into a test tube and add a drop of hydrochloric acid. Mix a drop of the obtained solution with 2-3 ml of water. Add a few drops of congo indicator to this very dilute solution of the acid: it turns bright blue (see Experiment 75). Add this blue solution, in small portions, to 2-3 ml of protein solution and note the change of colour.

B. Prepare a very dilute solution of sodium hydroxide following the procedure described in A. Add a few drops of phenolphthalein: the solution turns bright pink (not crimson). Place 2-3 ml of the starting protein solution into a clean test tube and add the dilute coloured alkali solution. Observe the change of colour.

Being an amphoteric electrolyte, protein (cf. Experiment 272), shows the buffer properties in solution form, i.e. it can bind both hydrogen and hydroxyl ions. The colour of congo indicator solution turns from blue to red (the acidity is reduced), and the pink colour of phenolphthalein disappears (the alkalinity of the system decreases). The amphoteric properties of protein, which reacts like a base in Test A and like an acid in Test B, are especially manifested in this Experiment.

275
Acid Properties of Protein

REAGENTS

White wool, thread or fabric.
Fuchsin.

Wash the woollen fabric in warm water with soap, rinse well, and press out the liquid.

Prepare 8-10 ml of very dilute solution of fuchsin in water. It must be intensely coloured but clear. Add 1-2 ml of concentrated ammonia solution: in 5-7 minutes the fuchsin solution is almost completely decolourized. Place about half the volume into another test tube and add 3-4 drops of concentrated caustic alkali solution. Place a small (1-2 cm) piece of moist wool fabric (thread) into both solutions.

In a few minutes the fabric turns intense blue-violet in the alkali-free colourless solution. In the other solution the wool remains undyed.

The bright colour of fuchsin solutions is due to the presence in them of the salt of fuchsin with acid (see explanations to Experiment 234). Alkalis, including ammonium hydroxide, decolourize these solutions to isolate almost colourless pseudo-base of fuchsin.

In the conditions of this experiment, protein fibres of wool react with the pseudo-base and get coloured, although the solution remains colourless. It follows that the carboxyl groups of the wool protein produce a salt-like compound with the fuchsin base. If the dye is contained in a very small concentration (i.e. in the presence of a great excess of protein) the weakly ionized solution of ammonia does not interfere with the formation of this salt. And vice versa, a strongly ionized caustic alkali prevents the formation of the fuchsin salt with protein.

276
Salting Out Proteins from Solution

REAGENTS

Proteins, solutions.
Ammonium sulphate, saturated about 43 per cent solution.
Ammonium sulphate, powder.

Place 3-4 ml of protein solution in a test tube and add an equal volume of saturated solution of ammonium sulphate. Shake the mixture slightly: the solution becomes cloudy and flakes of globulins precipitate. Transfer about 1 ml of the cloudy liquid into a separate test tube and add 2-3 ml of water. Shake the mixture: the protein precipitate dissolves again.

Pass the main bulk of the cloudy liquid through a dry pleated filter. Divide the clear filtrate into two parts. Heat one of them to boiling: the dissolved protein coagulates (cf. Experiment 277). Flakes precipitate or cloudiness develops. Add about 1-2 g of ammonium sulphate powder to the other part of the filtrate with slightly shaking the mixture until the powder no longer dissolves. The liquid above the small precipitate of salt crystals becomes cloudy or flakes of salted-out protein precipitate. Add a double volume of water: the precipitate re-dissolves.

Myosin solution almost does not contain albumins, and therefore the experiment ends at the stage of formation of a protein clot on the addition of saturated ammonium sulphate solution. As water is then added, the salted-out myosin re-dissolves poorly.

Salts of alkali metals and also of ammonium and magnesium (provided their concentration is sufficiently high) precipitate (salt

out) many proteins from their solutions. The cause of such salting out is that the electrical charge on the colloid particles of protein is eliminated by the oppositely charged salt ions which are adsorbed on proteins. Another cause is the removal of the hydrate membranes from the hydrophilic particles of proteins by the strongly hydrating ions of the salt added in large quantities. Both mentioned factors markedly lessen the stability of colloid solution since they facilitate sticking together and coagulation of protein particles and thus precipitate protein.

Ammonium sulphate is an especially effective salting-out agent. It precipitates proteins in both weakly acid and neutral medium. Salting out with other salts, e.g. chlorides and sulphates of sodium and magnesium, requires acidification of solution (cf. Experiment 272). Slight acidification of the medium sharply accelerates the salting-out process with ammonium sulphate as well.

Various proteins are salted out at different rates. When an equal volume of saturated ammonium sulphate solution is added to a solution of protein, the concentration of ammonium sulphate in the resultant solution is reduced two times. Globulins precipitate from such a 'half-saturated' ammonium sulphate solution and can be separated from albumins that remain in solution. A fully saturated solution of ammonium sulphate salts out both globulins and albumins.

Precipitation of proteins with salts of alkali metals and magnesium does not denature proteins, i.e. their molecular structure remains unchanged. The salting out is therefore a reversible process, and the precipitates are re-dissolved on addition of water.

277
Coagulation of Proteins by Heat

REAGENTS

Proteins, solutions.
Ammonium sulphate, 15 per cent solution.

Place 2-3 ml of protein solution in a test tube, heat over a burner and boil for 0.5-1 minute. Most proteins precipitate on boiling (the solution becomes cloudy or flakes precipitate). Slightly cool the liquid, divide it into two parts, and add 1-2 drops of concentrated acetic acid to one part and 1-2 drops of ammonium sulphate solution to the other. Heat both mixtures again until they start boiling: the quantity of coagulated protein markedly increases in both test tubes.

Slightly cool the mixtures. Add with shaking, first an equal volume of water and then 1 ml of dilute alkali solution to one test tube. The flakes of the coagulated protein do not dissolve in water and do quickly in alkali. As the alkaline solution is then boiled the protein does not coagulate.

A gelatin solution does not coagulate on boiling, even in the presence of salt.

Coagulation of proteins (their precipitation from solution on boiling) is characteristic of most representatives of compounds of this class. They most easily coagulate in a weakly acid medium in the vicinity of the isoelectric point (see Experiment 272), worse in a neutral medium, and usually do not coagulate in an alkaline medium. Casein, which is an acid, is present in a neutral solution in the form of a salt, and slight acidification is needed to coagulate it by boiling. Neutral salts, e.g. ammonium sulphate, sodium chloride, facilitate and accelerate coagulation of proteins by boiling. Sugars, polyhydric alcohols, many aldehydes, ketones, and amines protect proteins from coagulation.

Precipitation of protein by coagulation is irreversible and the precipitates fail to be dissolved in water or salt solutions. Coagulation of proteins by boiling is explained by the ability of large molecules of protein to change their structure (to be denatured) at 80-100 °C. As a protein molecule is consecutively split, for instance, by hydrolysis, the ability to coagulation weakens and then fully disappears. Peptones and albumoses, as well as some proteins of the primitive structure, for instance, gelatin, do not coagulate on boiling. A neutral solution of gelatin easily turns into a jelly on cooling. If a gelatin solution is boiled for a long time, its ability to form a jelly is lost.

278
Precipitation of Proteins with Concentrated Mineral Acids

REAGENTS

Proteins, solutions.

Place 1 ml of concentrated nitric acid and 1-2 ml of concentrated hydrochloric acid into two separate test tubes. Incline them and add, by the wall (as not to mix with the heavy acid layer), 1-1.5 ml of protein solution. Put the test tubes in the stand. A white circle of a protein precipitate is formed immediately, or gradually, at the interface. Shake the test tubes: the quantity of the precipitate

produced by nitric acid markedly increases, while the proteins precipitated by hydrochloric acid are dissolved in excess acid.

Gelatin is not precipitated by mineral acids in the described conditions.

Concentrated mineral acids react with proteins to give salt-like compounds with the amino group of the protein molecule. They also denature irreversibly protein and precipitate it. In most cases the precipitate is soluble in excess acid (except precipitates produced by nitric acid).

Among phosphoric acids, it is only metaphosphoric acid, HPO_3, that precipitates protein in the described conditions (even in dilute solutions). Metaphosphoric acid can thus be detected in the presence of other phosphoric acids (ortho- and pyro-phosphoric acids, H_3PO_4 and $H_4P_2O_7$, respectively) by this method.

Strong organic acids, trichloroacetic (see Table 5 and Experiment 75) and 5-sulphosalicylic acids are often used to precipitate proteins.

279
Precipitation of Proteins with Salts of Heavy Metals

REAGENTS

Proteins, solutions.
Copper sulphate, saturated solution.
Lead acetate, 20 per cent solution.

Place 1-1.5 ml of a protein solution into two separate test tubes and add copper sulphate into one, and lead acetate solution into the other test tube. Add the reagents slowly, drop by drop, and with shaking. Flakes precipitate, or the solutions become cloudy because sparingly soluble compounds of protein with the copper salt (blue) or lead salt (white) are first formed. As the reagents are further added, the precipitate is dissolved.

Even in very small concentrations, salts of heavy metals precipitate proteins to give salt-like compounds insoluble in water. Proteins are therefore antidotes in cases of poisoning with many heavy metal salts, for instance, salts of mercury (cf. Experiment 280).

Precipitation of proteins with salts of heavy metals is irreversible. However, some precipitates (like in the case described in this experiment) are dissolved in excess precipitant, i.e. in solutions of salts of copper, lead, or silver. This happens because the protein precipitates are peptized by ions adsorbed on their particles.

280
Precipitation of Proteins with Reagents for Alkaloids

REAGENTS

Proteins, solutions.
Picric acid, saturated solution.
Tannin, 10 per cent solution.
Potassium mercuric iodide, solution (see Experiment 248).

Place 1-1.5 ml portions of a protein solution into three separate test tubes. Add an equal volume of picric acid into one test tube: a yellow precipitate falls out. (If the protein concentration is small the solution becomes cloudy.)

Add 1-2 drops of concentrated acetic acid and 3-4 drops of tannic acid into the other test tube: a bulky precipitate of flakes falls out.

Add 1-2 drops of dilute hydrochloric acid and a few drops of potassium mercuric iodide into the third test tube: a precipitate falls out.

Precipitation of proteins with the reagents for alkaloids reveals the presence in the molecules of proteins of the nitrogen-containing groups (amino groups, heterocycles) that are characteristic of alkaloids (cf. Experiment 248). The precipitation is easier in a weakly acid medium, since in this case protein cations are predominantly formed (cf. Experiment 272), and protein reacts like a base similar to alkaloids because it contains heterocyclic groupings in the amino-acid residues and their combinations. A substance precipitated with tannic acid dissolves in an excess of the acid.

281
Denaturation of Proteins with Phenol and Formaldehyde

REAGENTS

Egg protein or *gelatin*, neutral solution (see the beginning of the chapter).
Dry gelatin, 50 × 8 mm strips.
Phenol, saturated solution.
Formaldehyde, 30-40 per cent solution.

A. Add phenol, drop by drop, to 1-2 ml of egg protein solution and observe the changes.

B. Place 1-1.5 ml of formaldehyde into a test tube and add an equal volume of water. Shake the solution, place a strip of gelatin (so that only its lower end is immersed in the liquid), and allow

to stand for 15-20 minutes. Discard the liquid and add hot water to cover the entire gelatin strip. Note the different character of swelling and dissolution of the lower and the upper end of the gelatin strip.

Proteins react with phenol and formaldehyde to give sparingly soluble products of condensation. The reaction proceeds with participation of free amino groups contained in the molecule of protein. Phenol quickly precipitates protein from solution to make it cloudy or to precipitate flakes or clots. Formaldehyde tans protein to consolidate it and to strongly reduce its swelling and solubility in water. Protein is denatured in both cases (cf. Experiment 277). Denaturation of proteins in plasma of living microorganism cells accounts for the disinfecting power of phenol and formaldehyde.

282
Biuret Reaction of Proteins

REAGENTS

Proteins, solutions.

A. Place 1-2 ml of protein solution in a test tube and add an equal volume of concentrated alkali solution. Now add a drop (not more) of copper sulphate solution: the liquid turns bright violet. The colour is detectable even in a coloured aqueous extract of meat.

B. If the concentration of protein (leukosin or milk albumin) in the solution is small, and the colour is insufficiently bright and distinct, mix in another test tube, a new portion of the protein with alkali solution. Incline the test tube and add carefully, from a pipette, 0.5-1 ml of copper sulphate solution so that it forms a supernatant layer without mixing with the main liquid. A distinct clear violet circle forms at the interface.

The biuret reaction (see Experiment 118) reveals the presence in the protein molecule of the peptide groups —CO—NH—. The products of protein decomposition, polypeptides, also give the biuret reaction, the colour of the forming copper complexes being dependent on the number of amino acids bound by the peptide bond. Dipeptides give blue colouration, tripeptides, violet, and tetrapeptides and more complicate peptides, give red colour.

Some other atomic groupings, e.g. —CS—NH—, —CH—NH—, when they are accumulated in the molecule, can also give the biuret reaction. In carrying out the biuret reaction, excess copper salt should be avoided, since the blue cupric hydroxide that is formed in this case masks the violet colouration. Explanations to Experiment 120 give more detail on the colour reactions in the form of a circle.

283
Reaction of Proteins with Millon's Reagent

REAGENTS

Proteins, solutions.
Millon's reagent.

To prepare Millon's reagent, dissolve with heating 2 g (0.15 ml) of mercury in 3 ml of concentrated nitric acid, and dilute the solution to 10 ml. Allow the solution to stand for a few hours and decant the supernatant liquid from the precipitate, if any.

Place 0.5-1 ml of a protein solution in a test tube, add an equal volume of Millon's reagent, and heat the mixture (without shaking) on a boiling water bath. White flakes that first precipitate stick together into characteristic brick-red clots on heating. The solution can sometimes turn red as well.

Millon's reagent acts on protein to give first a white mercury compound (see Experiment 280). The precipitate is then coloured pink or red only on the conditions that the starting protein contains residues of tyrosine or tryptophan in its molecule. Tyrosine (beta-para-hydroxyphenylalanine) contains the phenol hydroxyl. Tryptophan (beta-indolylalanine) is a heterocyclic compound. Some proteins, for instance, pure gelatin, almost do not contain tyrosine or tryptophan and therefore do not give the characteristic colouration in the reaction with Millon's reagent. At the same time, many phenols give this characteristic colour reaction in the absence of proteins. The distinctness of the reaction decreases in the presence of some inorganic compounds, such as hydrogen peroxide, chlorides and other salts.

The nature of the formed red products has not been well studied. In order to ensure a successful reaction, Millon's reagent should contain a certain amount of free nitrogen oxides.

284
Xanthoprotein Reaction

REAGENTS

Proteins, solutions.

Place 1 ml of protein solution in a test tube and add 0.2-0.3 ml of concentrated nitric acid: a white precipitate falls out or the solution becomes cloudy (cf. Experiment 278). Heat the mixture on a burner and boil for 1-2 minutes: the solution and the precipitate

turn bright yellow. The precipitate may partly or fully dissolve on boiling as a result of hydrolysis but the characteristic yellow colour of the solution persists. Cool the acid mixture and carefully add, drop by drop, an excess (1-2 ml) of concentrated alkali solution. Acid albuminate that first precipitates reacts with excess alkali to give a bright orange solution.

The xanthoprotein reaction reveals the presence in protein of single or condensed aromatic nuclei, which are the residues of such acids as phenylalanine, tyrosine, or tryptophan. The yellow colour is the result of nitration of these nuclei with nitric acid and formation of polynitro compounds. The formation of intensely coloured anions (cf. Experiments 172 and 173) accounts for the change of the yellow colour of these substances to red in alkaline solution.

Aqueous ammonia can be used instead of caustic alkali.

Acid albuminates that are formed by the energetic action of acids on proteins are insoluble in water or dilute salt solutions, but are readily soluble in alkalis and dilute acids. Acid albuminates bind much greater quantities of alkali than does the starting protein.

Pure gelatin does not contain many of the above named amino acids and does not therefore give the xanthoprotein reaction.

285
Glyoxylic Reaction of Proteins (Adamkiewicz-Hopkins Test)

REAGENTS

Proteins, solutions.
Glyoxylic acid, solution.

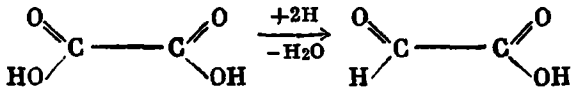
To prepare a solution of glyoxylic acid salt, add about 1 ml of sodium amalgam to 5-7 ml of saturated solution of oxalic acid and allow the mixture to stand for an hour. Decant the aqueous solution and use it in the experiment.

To prepare sodium amalgam, place 1-2 ml of dry mercury (dry the metal surfaces with filter paper) into a small porcelain mortar, add a grain of sodium (not more than the size of a half-pea). Perform this operation behind a glass door of the HOOD. Sodium should be first cleaned from crust and kerosene in which it is kept. Using a pestle, press sodium into mercury, down to the bottom of the mortar. It dissolves in mercury, sometimes with a flash. Add new (the second and the third) portions of sodium. The amalgam is liquid if it contains below 1 per cent of sodium. At higher sodium concentrations it thickens on cooling and solidifies. Keep the amalgam in a stoppered vessel.

Place 0.5-1 ml of protein solution in a test tube, add 2 ml of glacial acetic acid and 0.5 ml of glyoxylic acid salt solution. Shake the mixture and carefully add 2 ml of concentrated sulphuric acid, pouring it by the wall of the test tube so that the layers do not mix.

A red circle appears at the interface. The circle is sometimes composed of several layers and has bluish and greenish tints, which are well distinguishable against a white background. If the circle fails to appear, carefully swing the test tube and slightly heat over a burner on its one side.

The glyoxylic reaction (Adamkiewicz-Hopkins test) is characteristic only of proteins that contain tryptophan (cf. Experiments 283 and 284). Tryptophan reacts with glyoxylic acid, HOOC—C(=O)H, to give coloured condensation products. Glyoxylic acid is sometimes contained in acetic acid in quantities sufficient to give the colour reaction. It is, however, more convenient to add glyoxylic acid itself. It is prepared by reducing oxalic acid with sodium amalgam:



Gelatin does not contain tryptophan and does not therefore give this reaction.

286
Splitting of Protein by Alkali

REAGENTS

Proteins, solutions.
Lead nitrate, or *acetate*, 10 per cent solution.

Place 1-2 ml of protein solution into a test tube, add two volumes of concentrated alkali solution, and boil 2-3 minutes: a precipitate (sometimes insignificant) falls out. On further boiling the precipitate dissolves to liberate ammonia that can easily be detected by odour, provided the protein concentration in solution is not very small. Ammonia is especially easy to detect when egg protein, casein, or aqueous extract of meat are boiled with alkali.

Add 1 ml of lead salt to the hot alkaline solution and boil again: a white precipitate of lead hydroxide that first precipitates dissolves in excess alkali. If protein reacts with alkali to eliminate sulphur, lead sulphide is formed and the clear solution gradually turns brown. If the sulphur content is relatively high, a dark brown or black precipitate of lead sulphide falls out.

The energetic action of caustic alkalis on proteins changes them deeply. In addition to partial hydrolysis, the site of which is the peptide linkage, part of amino groups is eliminated in the form of ammonia. If a protein contains cystine or cysteine in its molecule, these amino acids also eliminate gradually sulphur in the form of hydrogen sulphide that converts into metal sulphide in an alkaline medium. The coloured lead sulphide is insoluble in alkalis and is easy to detect

$$Pb^{2+} + 4OH^- \longrightarrow PbO_2^{2-} + 2H_2O$$

$$S^{2-} + PbO_2^{2-} + 2H_2O \longrightarrow PbS + 4OH^-$$

Caustic alkalis react with proteins to give alkaline albuminates that strongly differ from the starting protein both with respect to their composition and properties. They have acid character, readily dissolve in alkali solutions and dilute acids, and fail to be precipitated from alkaline solutions by boiling or salting out.

Unlike most proteins, gelatin almost does not contain sulphur.

APPENDIX

List of Commonly Used Reagents and Indicators

Reagent	Solution concentration			Density, g/cc	Method of preparing
	% (w/w)	g/100 ml	*N*		
1	2	3	4	5	6
Hydrochloric acid					
concentrated	34-37	41-44	11-12	1.17-1.18	
dilute	6-7	6-7	2	1.03	Dilute concentrated acid in 5 volumes of water
Sulphuric acid					
concentrated	92-98	170-180	34-36	1.83-1.84	
dilute	15	~ 17	3.5	1.11	Dilute concentrated acid in 10 volumes of water
Nitric acid					
concentrated	60-68	82-95	13-15	1.37-1.40	
dilute	14	~ 15	2.3	1.08	Dilute concentrated acid in 5 volumes of water
Acetic acid					
concentrated (glacial)	98-100	105	~ 17	1.06	
dilute	~ 13	~ 13	~ 2	1.02	Dilute glacial acid in 7 volumes of water
Sodium hydroxide					
concentrated	33	45	11	1.36	Dissolve solid NaOH in two weights of water
dilute	~ 7	~ 8	~ 2	1.08	Dilute concentrated alkali solution in 5 volumes of water
Potassium hydroxide					
concentrated	33	43-44	~ 8	1.32	1 part of solid KOH per 2 parts by weight of water
dilute	10	~ 11	~ 2	1.08	1 volume of concentrated solution per 3 volumes of water
Ammonia solution					
concentrated	22-27	20-25	12-14	0.90-0.92	
dilute	3-5	3-5	2	~ 0.98	Dilute concentrated solution in 5 volumes of water

Continuation

Reagent	Solution concentration			Density, g/cc	Method of preparing
	% (w/w)	g/100 ml	*N*		
1	2	3	4	5	6
Sodium carbonate	5	~ 5	1	1.05	Dissolve 50 g of anhydrous soda or 135 g of $Na_2CO_3 \cdot 10H_2O$ in 1000 ml of water
Sodium bicarbonate	5	5	0.6	1.05	Dissolve 50 g of $NaHCO_3$ in 1000 ml of water
Ferric chloride	1.6	1.6	0.3	1	Dissolve 27 g of $FeCl_3 \cdot 6H_2O$ in 1000 ml of water; add 15 ml of concentrated HCl
Copper sulphate	5	5	0.7	1.05	Dissolve 80 g of $CuSO_4 \cdot 5H_2O$ in 1000 ml of water
Silver nitrate	1	1	0.06	1	Dissolve 10 g of $AgNO_3$ in 1000 ml of water; keep in dark bottle
Potassium permanganate	1	1	~0.3 (acid) ~0.2 (alk)	1	Dissolve 10 g of $KMnO_4$ in 1000 ml of water; keep in dark bottle
Bromine solution in $CHCl_3$ or CCl_4	2	3	0.4	1.5 (1.6)	Dissolve 1 ml of bromine in 100 ml of solvent
Bromine water	1	1	0.13	1.02	Dilute 100 ml of saturated aqueou solution of bromine in 200 ml of water
Iodine	1	1	0.1	1.07	Dissolve 10 g of iodine and 50 g of KI in 200 ml of water; add water to 1000 ml
Potassium iodide	5	5	0.3	1.06	Dissolve 50 g of KI in 1000 ml of water
		Indicators			
Phenolphthalein					Dissolve 0.2 g in a mixture of 165 ml of alcohol and 135 ml of water
Methyl orange					Dissolve 0.5 g in 500 ml of water
Congo					Dissolve 0.5 g in 20 ml of alcohol; add water to 1000 ml

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